UNDERSTANDING LONG-RANGE TRANSPORT MECHANISMS OF PERFLUOROALKYL SUBSTANCES

by

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Abstract

Perfluoroalkyl acids (PFAAs) are persistent, bioaccumulative compounds found ubiquitously within the environment. They can be formed from the atmospheric oxidation of volatile precursor compounds and undergo long-range transport (LRT) through the atmosphere and ocean to remote locations. Ice caps preserve a temporal record of PFAA deposition making them useful in studying the atmospheric trends in LRT of PFAAs as well as understanding major pollutant sources and production changes over time.

A 15 m ice core representing 38 years of deposition (1977 – 2015) was collected from the Devon Ice Cap in Nunavut and analyzed for PFAAs. Samples were concentrated by solid phase extraction and analyzed by UPLC-MS/MS, IC, and ICP-OES. Both short- and long-chain perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) were detected in the samples, with fluxes ranging from <LOD to 4.44×10^{4} ng m^{-2} yr^{-1}.

In this work I assess temporal trends in deposition, homologue profiles, ion tracers, air mass transport models, and production and regulation trends to characterize the PFAA depositional profile on the Devon Ice Cap and to further understand the LRT mechanisms of these persistent pollutants. In Chapter 3 my results demonstrate that the PFCAs and perflurooctane sulfonate (PFOS) have continuous and increasing deposition on Devon Ice Cap, despite recent North American regulations and phase-outs. I propose that this is the result of on-going emission and use of these compounds, their precursors and other newly unidentified compounds in regions outside of North America. Through modelling air mass transport densities, and comparing temporal trends in deposition with

production changes of possible sources, I find that Eurasian sources, particularly from Continental Asia are large contributors to the global pollutants impacting Devon Ice Cap. By comparing PFAAs to their precursors and correlating pairs of PFCAs, I determine that deposition of PFAAs is dominated by atmospheric formation from volatile precursor sources, and major ion analysis provides new information regarding the transport of PFAAs, confirming that marine aerosol inputs are unimportant to the LRT mechanisms of these compounds. In Chapter 4 my results from the Arctic ice core analysis show a ten-fold increase in short-chain PFCA (scPFCA) deposition between 1986 and 2014, which coincides with increased production and atmospheric burden of chlorofluorocarbon (CFC)-replacement compounds. This is the first multi-decadal temporal record of scPFCA deposition and indicates that Montreal Protocol-mandated introduction of CFC-replacement compounds for the heat-transfer industry is the dominant source of scPFCAs to remote regions.

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List of Abbreviations, Nomenclature and Symbols

°C	degrees celsius
AERS	Anions Electrolytically Regenerated Suppressor
AFFFs	aqueous film forming foams
AMSL	above mean sea level
APFN	ammonium perfluorononanoate
APFO	ammonium perfluorooctanoate
CCIW	Canadian Center for Inland Waters
CFC	chlorofluorocarbon
cm	centimetre
COF_2	carbonyl fluoride
ECF	electrochemical fluorination
EE	extraction efficiency
EU	European Union
FOSA	perfluorooctanesulfonamide
FTACs	fluorotelomer acrylates
FTALs	fluorotelomer aldehydes
FTCAs	fluorotelomer carboxylic Acids
FTIs	fluorotelomer iodides
FTOHs	fluorotelomer alcohols
FTOs	fluorotelomer olefins
g	gram
HCFCs	hydrochlorofluorocarbons
HF	hydrogen fluoride
HFCs	hydrofluorocarbons
HFEs	hydrofluoroethers
HFOs	hydrofluoroolefins
HNO_3	nitric acid
HO_2	hydroperoxyl radical
HPLC	high-performance liquid chromatography
HYSPLIT	HYbrid Single Particle Lagrangian Integrated Trajectory
IAEA	International Atomic Energy Agency
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICS	ion chromatography system
IDL	instrument detection limit
IP	instrument performance standard

IS	internal standard
K_{AW}	air-water partition coefficient
kg	kilogram
K_{OC}	organic carbon-water partition coefficient
K_{OW}	octanol-water partition coefficient
kt	kilotonnes
kV	kilovolt
L	litre
LLGHGs	long-lived greenhouse gases
LOD	limit of detection
LOQ	limit of quantitation
LRT	long-range transport
m	metre
m/z	mass-to-charge ratio
MAC	mobile air-conditioning
MDL	method detection limit
ME	matrix effects
MeOH	methanol
mg	milligram
mL	millilitre
mm	millimetre
mM	millimolar
MRM	multiple reaction monitoring
NAFSAs	N-alkyl perfluoroalkane sulfonamides
NAFSEs	N-alkyl perfluoroalkane sulfonamidoethanols
NCAR	National Center for Atmospheric Research
NCEP	National Center for Environmental Protection
ng	nanogram
NH_4OH	ammonium hydroxide
NO	nitric oxide
NOAA	National Oceanic and Atmospheric Administration
NO_x	nitrogen oxides
nss	non-sea salt
O_3	ozone
ODP	ozone depleting potential
ODSs	ozone-depleting substances
OH•	hydroxyl radical
Pa	pascal
PASFs	perfluoroalkane sulfonyl fluorides

Pb	lead
PBSF	perfluorobutane sulfonyl fluoride
PFAAs	perfluoroalkyl acids
PFAIs	perfluoroalkyl iodides
PFALs	perfluorinated aldehydes
PFASs	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutanesulfonic acid
PFCAs	perfluorocarboxylates/ perfluoroalkyl carboxylic acids
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFDS	perfluorodecanesulfonic acid
PFECHS	perfluoroethylcyclohexanesulfonate
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptanesulfonic acid
PFHxA	perfluorohexanoic acid
PFHxDA	perfluorohexadecanoic acid
PFHxS	perfluorohexanesulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOcDA	perfluorooctadecanoic acid
PFOS	perfluorooctanesulfonic acid
PFOs	perfluoroolefins
PFPeA	perfluoropentanoic acid
PFPrA	perfluoropropionic acid
PFSAs	perfluoroalkylsulfonates/ perfluoroalkyl sulfonic acids
PFTeDA	perfluorotetradecanoic acid
PFTrDA	perfluorotridecanoic acid
PFUnDA	perfluoroundecanoic acid
pg	picogram
pKa	acid dissociation constant
POPs	persistent organic pollutants
POSF	perfluorooctane sulfonyl fluoride
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
QA/QC	quality assurance quality control

REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RF	radio frequency
RO_2	peroxy radical
rpm	revolutions per minute
RSD	relative standard deviation
S/N	signal-to-noise ratio
scPFCAs	short-chain perfluoroalkyl carboxylic acids
SD	standard deviation
SLAP	Standard Light Antarctic Precipitation
SNUR	Significant New Use Rules
SPE	solid phase extraction
SSA	sample spike after
SSB	sample spike before
SSML	sea surface microlayer
SVHC	Substances of Very High Concern
TAC-ULP1	ultra low pressure trace anion concentrator column
TFA	trifluoroacetic acid
TFE	tetrafluoroethylene
U.S.	United States
UPLC-MS/MS	ultra performance liquid chromatography tandem mass spectrometry
US EPA	United States Environmental Protection Agency
US FDA	United States Food and Drug Administration
UV	ultraviolet
V	volt
VSMOW	Vienna Standard Mean Ocean Water
W	watts
w/w	weight per weight
WAX	weak anion exchange
WWTPs	wastewater treatment plants
xFOSEs	N-methyl and N-ethyl perfluorooctane sulfonamidoethanol
yr	year
µg	microgram
µL	microlitre
µm	micrometre

List of Appendices

Co-authorship Statement

This thesis is comprised of two manuscripts that are in preparation for submission to be published in peer-reviewed scientific journals. It should be noted that Chapter One comprises the introduction to this thesis, while Chapter Two comprises the methodologies for both manuscripts summarized in Chapters Three and Four. All manuscripts were written by Heidi M. Pickard, with critical comments by Cora J. Young and Amila O. De Silva and editorial comments by Chris Rowley. The contributions of co-authors are detailed below:

Chapter One – Introduction and Overview

Contributions – Prepared by Heidi M. Pickard with editorial comments provided by Cora J. Young and Amila O. De Silva.

Chapter Two - Methodology

Contributions - Prepared by Heidi M. Pickard with editorial comments provided by Cora J. Young and Amila O. De Silva. Sample collection and dating of the ice core was carried out by Alison S. Criscitiello and Martin J. Sharp, with assistance by Colleen Mortimer and Anja Rutishauser. Ice core sectioning was a team effort, done by Heidi M. Pickard, Cora J. Young, John MacInnis and Cyril Cook. During this process, Heidi M. Pickard measured and packaged the ice core sections, John MacInnis handled the ice cores, Cyril Cook handled the saw, and Cora J. Young recorded the data. Sample extraction was performed by Heidi M. Pickard, with training from Christine Spencer and assistance from John MacInnis. Sample analysis for the long-chain PFCAs and PFSAs

was prepared by Heidi M. Pickard and run on the UPLC-MS/MS by Christine Spencer. Data interpretation was conducted by Heidi M. Pickard, following training by Christine Spencer. Short-chain PFCA method development and analysis was carried out by Christine Spencer and Amila O. De Silva. Major ion analysis using the ICS was carried out by Heidi M. Pickard, with training and assistance from Trevor VandenBoer and Jamie Warren, while ICP-OES analysis was done by the Newfoundland and Labrador Department of Natural Resources.

Chapter Three - Continuous Non-Marine Inputs of Per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record

Author List – Heidi M. Pickard, Alison S. Criscitiello, Christine Spencer, Martin J. Sharp, Derek C. G. Muir, Amila O. De Silva, Cora J. Young.

Contributions – See Chapter 2: Methodology Contributions for above Author List. Data analysis was performed by Heidi M. Pickard, with critcial contributions from Cora J. Young and Amila O. De Silva. Data interpretation and manuscript preparation was completed by Heidi M. Pickard with critical comments provided by Cora J. Young and Amila O. De Silva.

Chapter Four - Persistent Fluorinated Compounds Increasing in the Arctic as a Result of the Montreal Protocol

Author List – Heidi M. Pickard, Alison S. Criscitiello, Christine Spencer, Martin J. Sharp, Derek C. G. Muir, Amila O. De Silva, Cora J. Young.

Contributions – See Chapter 2: Methodology Contributions for above Author List. Christine Spencer and Amila O. De Silva developed the method and analysis for the

short-chain PFCAs. Data analysis was performed by Heidi M. Pickard, with critcial contributions from Cora J. Young and Amila O. De Silva. Data interpreation and manuscript preparation was completed by Heidi M. Pickard with critical comments provided by Cora J. Young and Amila O. De Silva, and input from Alison S. Criscitiello and Derek C. G. Muir.

1 Introduction and Overview

1.1 Per- and Polyfluoroalkyl Substances

Per- and polyfluoroalkyl substances (PFASs, C_nF_{2n+1}-R) are widely used anthropogenic chemicals found ubiquitously within the environment. PFASs have been used in surfactants and polymers for commercial and industrial applications since the 1950s. They are a diverse group of highly fluorinated aliphatic compounds that differ in both their functional groups (-R = $-COO^-$, $-SO_3^-$) and carbon chain lengths (C_nF_{2n+1} = 1-17). The properties of thermal and chemical stability of the perfluoroalkyl moiety (C_nF_{2n+1}-), as well as their hydrophobic and lipophobic nature make them very useful for a variety of applications.[1] These applications include use as stain-resistant coatings for textiles and other surfaces, use as polymerization aids and use in fire fighting foams (aqueous film forming foams, AFFFs).[2]

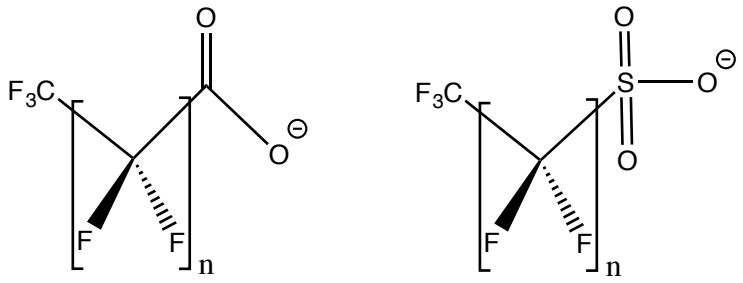
There are a number of sub-groups of perfluoroalkyl substances, in which all of the carbon atoms of the alkyl chain are fully fluorinated. These sub-groups include the perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), perfluorosulfonamides and sulfonamide ethanols, fluorotelomer alcohols (FTOHs), and saturated and unsaturated fluorotelomer acids. Two of the most commonly investigated sub-groups are the PFCAs ($C_nF_{2n+1}COO^-$) and PFSAs ($C_nF_{2n+1}SO_3^-$), which are typically distinguished based on their chain-length (Figure 1.1). In the environment, less stable PFASs can degrade and transform into highly stable end products, such as the perfluoroalkyl acids (PFAAs), which have extraordinary environmental persistence. The

PFCAs and PFSAs are both members of the perfluoroalkyl acid (PFAA) family since they are strong acids and fully fluorinated.

The environmental impact of PFASs emerged as a concern in the early 2000s when certain PFCAs and PFSAs were found ubiquitously in various environmental and biological matrices, particularly human blood.[3,4] These compounds were also found to have effects on human health[5] and the aquatic environment.[6] Following these discoveries, many regulations have been implemented over the years to restrict the manufacture and use of certain PFASs.

1.1.1 Perfluoroalkyl Acid Properties

The environmental fate of all PFASs is determined by their different physicochemical properties, which will vary depending on their chain length and functional groups. The perfluoroalkyl acids themselves are persistent organic pollutants (POPs), but have different properties compared to traditional POPs. The PFAAs consist of a hydrophobic (perfluoroalkyl chain of varying length) and hydrophilic (carboxyl or sulfate) moiety. This duality gives rise to their surfactant properties by which they prefer to reside at the interfaces of sediment-water, air-water, and air-particle systems, as molecules and/or aggregates.[7] Long-chain PFCAs ($C_nF_{2n+1}COO^-$) refer to $n \geq 7$ and long-chain PFSAs ($C_nF_{2n+1}SO_3^-$) are $n \geq 6$, while short-chain PFAAs are $n < 7$ and $n < 6$, respectively. The short-chain PFCAs are commonly found in the dissolved phase, while the long-chain PFCAs and PFSAs tend to bind strongly to particles.[8]



(A) PFCAs (n=0-16) (B) PFSAs (n=3-9)

Figure 1.1. Chemical Structure of a) PFCAs and b) PFSAs.

PFAAs can exist as either linear (i.e. n-alkyl) or branched alkyl isomers (i.e. n-PFOS ($F(n\text{-}CF_2)_8SO_3^-$) versus iso-PFOS ($(CF_3)_2CF(CF_2)_5SO_3^-$)). The mixtures of linear and branched isomers can present challenges in accurately quantifying PFAAs in environmental matrices, but they can also aid in understanding sources of PFAAs.[9] The production of isomers varies by manufacturing process, with the telomerization process producing linear isomers based on polymerization of tetrafluoroethylene (TFE) ($CF_2=CF_2$) and the electrochemical fluorination (ECF) process producing a mixture of linear and branched isomers due to cleavage and rearrangements during the perfluorination reaction with hydrofluoric acid (HF).[1,10] The ratio of linear to branched in the ECF process is roughly 70-80% linear and 20-30% branched.[11]

In addition to their use in commercial products and consumer applications, PFAAs are also terminal degradation products from abiotic and biotic degradation of precursor PFASs. Numerous precursors to the PFCAs and PFSAs are summarized in Table 1.1.

Table 1.1. A list of PFAA precursor compounds and their chemical structures.[1,12]

Name	Acronym	Chemical Structure
Fluorotelomer Alcohols	FTOHs	$C_nF_{2n+1}CH_2CH_2OH$
Unsaturated Fluorotelomer Alcohols	FTUOHs	$C_nF_{2n+1}CF=CHCH_2OH$
Fluorotelomer Acrylates	FTAcs	$C_nF_{2n+1}CH_2CH_2OC(O)CH=CH_2$
Fluorotelomer Methacrylates	FTMACs	$C_nF_{2n+1}CH_2CH_2OC(O)C(CH_3)=CH_2$
Fluorotelomer Iodides	FTIs	$C_nF_{2n+1}CH_2CH_2I$
Fluorotelomer Olefins	FTOs	$C_nF_{2n+1}CH=CH_2$
Fluorotelomer Aldehydes	FTALs	$C_nF_{2n+1}CH_2CHO$
Unsaturated Fluorotelomer Aldehydes	FTUALs	$C_nF_{2n+1}CF=CHCHO$
Fluorotelomer Carboxylic Acids	FTCAs	$C_nF_{2n+1}CH_2COOH$
Unsaturated Carboxylic Acids	FTUCAs	$C_nF_{2n+1}CF=CHCOOH$
n:3 Saturated Acids	n:3 Acids	$C_nF_{2n+1}CH_2CH_2COOH$
n:3 Unsaturated Acids	n:3 UAcids	$C_nF_{2n+1}CH=CHCOOH$
Fluorotelomer Sulfonic Acids	FTSAs	$C_nF_{2n+1}CH_2CH_2SO_3H$
N-Alkyl Perfluoroalkane Sulfonamides	NAFSAs	$C_nF_{2n+1}SO_2NH(C_xH_{2x+1})$ (x=1,2,4)
N-Alkyl Perfluoroalkane Sulfonamidoethanols	NAFSEs	$C_nF_{2n+1}SO_2N(C_xH_{2x+1})CH_2CH_2OH$, ($x$=0,1,2,4)
N-Alkyl Perfluoroalkane Sulfonamidoacetic acids	NAFASAAs	$C_nF_{2n+1}SO_2N(C_xH_{2x+1})CH_2COOH$, ($x$=0,1,2,4)
Polyfluoroalkyl Phosphate Esters	PAPs	$(C_nF_{2n+1}CH_2CH_2O)_xP(=O)(OH)_{3-x}$, x=1,2
Perfluorooctane Sulfonyl Fluoride	POSF	$C_nF_{2n+1}SO_2F$
Hydrochlorofluorocarbons	HCFCs	$C_nF_{2n+1}CHFCl$ $C_nF_{2n+1}CH_xCl_y$ (x=1,2, y=1,2)
Hydrofluorocarbons	HFCs	$C_nF_{2n+1}(CHF)_xCH_yF_z$ $C_nF_{2n+1}(CHF)_x(CF_2)_yF$ (x=0,1,2, y=0,1,2,3, z=0,1,2,3)
Hydrofluoroethers	HFEs	$C_nF_{2n+1}O(CH_2)_xH$ (x=1,2)
Hydrofluoroolefins	HFOs	$C_nF_{2n+1}CF=CH_xF_y$ (x=0,1,2, y=0,1,2)
Fluorinated Anaesthetics (Halothane, Desflurane, Isoflurane)		$C_nF_{2n+1}CH(Cl_w)(Br_x)(F_y)(OCHF_2)_z$ (w=0,1, x=0,1, y=0,1, z= 0,1)

1.1.1.1 Physicochemical Properties

PFAAs are widely distributed in the global environment due to their solubility in water, low-to-moderate sorption to soils and sediments, and resistance to biological and chemical degradation.[7,13] PFCAs and PFSAs are ionized under most environmental conditions and will therefore reside in water. Despite their widespread occurrence, very little experimental data is available on the physicochemical properties of PFAAs in their

ionized form. This section will therefore only summarize the expected physicochemical properties of these compounds.

PFCAs and PFSAs have relatively high water solubility's (g L^{-1}) due to the hydrophilic carboxylate and sulfonate groups on the molecules.[14] The solubility of PFAAs is highest for short-chain PFAAs and decreases with molecular weight due to the increase in hydrophobic perfluorinated alkyl chain length. In natural waters (neutral pH), and under most environmental conditions, PFCAs and PFSAs will predominantly be present in their anionic form, due to their low acid dissociation constants (pKa).[15,16] Their water solubility in natural waters will strongly depend on ion composition, temperature and other factors. PFAAs have low pKa values (pKa < 1) since they are strong acids and usually exist as dissociated anions under most environmental conditions,[16] however there has been considerable debate regarding appropriate pKa values, especially for PFOA.[7] In some limited cases PFAAs can be present in their protonated form, which has different physicochemical properties. For example, the perfluorooctanoate anion is highly water-soluble and has negligible vapour pressure, whereas the protonated perfluorooctanoic acid has low water solubility and sufficient vapour pressure to partition out of water into air,[17] but this is very unlikely. Water solubility and acid dissociation constants for neutral PFAAs are summarized in Table 1.2.

The PFAAs themselves have very low vapour pressures compared to their precursor counterparts (e.g. FTOHs), which have varying but higher vapour pressures than PFAAs and are classified as volatile. Vapour pressures decrease with increasing perfluorinated chain length.[18] Wang et al.[7] summarizes vapour pressures and other data

for condensed to gas-phase partitioning (K_{OA} – octanol-air partitioning coefficient and K_{AW} – air-water partitioning coefficient), but only for the neutral PFAAs and their precursors. Vapour pressures for the neutral PFCAs and PFSAs are given in Table 1.2

The sorption and mobility of PFAAs can be estimated using different partitioning coefficients. The degrees to which PFAAs sorb to organic carbon in sediment and soils during transport in water are estimated by the organic-carbon partition coefficient (K_{OC}) and the octanol-water partition coefficient (K_{OW}).[14] However, K_{OW} values for ionized PFAAs are experimentally impossible to measure since they do not follow typical lipid partition dynamics and will accumulate at the interface, essentially forming another phase.[14] In general, sorption of PFAAs will increase with increasing perfluorinated chain length. Although limited in evidence, surface sorption of PFAAs to charged mineral surfaces is also considered to be an important mechanism for PFAA transport in water.[14] Wang et al.[7] summarize sorption partition coefficient values for the neutral PFAAs and their precursors. Partition coefficient values for K_{OC} are provided in Table 1.2 for the neutral PFCAs and PFSAs.

Table 1.2. Physicochemical properties of neutral PFCAs and PFSAs. Data from references [7,14] and references therein.

Name	Acronym	Water Solubility ($g\ L^{-1}$)[14]	Vapour Pressure (Pa)[7,14]	log K_{OC} ($L\ kg^{-1}$)[14]	Dissociation Constant (pKa)[14]
Perfluoroalkyl Carboxylic Acids	PFCAs				
Perfluorobutanoic Acid	PFBA	Miscible	1307	1.88	−0.2 – 0.7
Perfluoropentanoic Acid	PFPeA	112.6	1057	1.37	−0.06
Perfluorohexanoic Acid	PFHxA	21.7	457	1.91	−0.13
Perfluoroheptanoic Acid	PFHpA	4.2	158	2.19	−0.15
Perfluorooctanoic Acid	PFOA	3.4 – 9.5	4 – 1300	1.31 – 2.35	−0.16 – 3.8
Perfluorononanoic Acid	PFNA	9.50	1.3	2.39	−0.17
Perfluorodecanoic Acid	PFDA	9.50	0.2	2.76	−0.17
Perfluoroundecanoic Acid	PFUnDA	0.004	0.1	3.30	−0.17
Perfluorododecanoic Acid	PFDoDA	0.0007	0.01	NA[1]	−0.17 – 0.8
Perfluorotridecanoic Acid	PFTrDA	0.0002	0.3	NA	NA
Perfluorotetradecanoic Acid	PFTeDA	0.00003	0.1	NA	NA
Perfluoroalkyl Sulfonic Acids	PFSAs				
Perfluorobutanesulfonic Acid	PFBS	46.2 – 56.6	631	1.00	−6.0 to −5.0
Perfluorohexanesulfonic Acid	PFHxS	2.3	58.9	1.78	−6.0 to −5.0
Perfluorooctanesulfonic Acid	PFOS	0.52 – 0.57	6.7	2.5 – 3.1	−6.0 to −2.6
Perfluorodecanesulfonic Acid	PFDS	0.002	0.71	3.53	NA

[1]NA – Data not available/not applicable

1.1.1.2 Toxicity and Exposure

PFAAs will bind to proteins and phospholipids, and are found at elevated concentrations in tissues with high protein and phospholipid content (e.g. liver, kidney, blood, etc.).[19] Due to their chemical stability and resistance to biological degradation, they will persist in the environment and undergo bioaccumulation (i.e. $[PFA]_{predator} + [PFA]_{prey}$). Certain PFAAs (>7 perfluorocarbons) will undergo biomagnification (i.e. concentration gradient across an entire food web). The long-chain PFAAs are generally more bioaccumulative than the short-chain analogues and more likely to biomagnify into the food web, but for very large PFAAs (i.e. >12 perfluorocarbons), bioaccumulation is less due to limited bioavailability.[20]

PFAA uptake can occur by oral, inhalation or dermal exposure. For PFCAs, once exposed, approximately 90 – 99% of the compound in the blood will bind to serum albumin.[21] There is no evidence to indicate that long-chain PFAAs will metabolize in mammals and thus elimination can only be achieved by excretion. Perfluorooctanesulfonic acid (PFOS, 8 perfluorinated carbons), the most-studied long-chain PFSA, is excreted more slowly than perfluorooctanoic acid (PFOA, 7 perfluorinated carbons), the most-studied long-chain PFCA, and thus PFOA has a shorter elimination half-life and higher rate of excretion.[22] The PFOS half-life in humans is 5.4 years, while the PFOA half-life is 3.8 years.[23] It has also been shown that branched isomers are excreted more rapidly than the linear isomers, which tend to accumulate more, and short-chain PFAAs excrete more rapidly than long-chain PFAAs.[22]

The toxicity of PFAS is an emerging field. PFOS and PFOA have been shown to have moderate acute toxicity in routine toxicological assays.[22] PFOS and linear isomers are more toxic than PFOA and branched isomers, and can cause adverse effects at lower dosages, such as a decreased rate of excretion.[24] Numerous publications have studied the biological properties of PFAAs, but are mostly limited to PFOS and PFOA.[22] These two PFAAs have been toxicologically examined in many animal studies, and show that the subacute and subchronic effects of PFOS and PFOA vary depending on species,[22] but generally show developmental toxicity, immunotoxicity, hepatoxicity, neurotoxicity, tumor induction, endocrine disruption, and other carcinogenic effects at high doses. There is emerging evidence that PFAS are more toxic to the second generation, which deviates from traditional toxicological approaches. In addition, various animal models have

indicated sex-specific pharmacokinetics and thus new ventures into evaluating toxicity of PFAS are cognizant of species, sex, and multigenerational effects.

1.1.2 Perfluoroalkyl Acids in the Environment

Due to their physicochemical properties, persistence and ability to be formed from precursor compounds, PFAAs are found ubiquitously in the environment. They have been detected in many environmental matrices, in urban, industrialized and remote locations worldwide. Many monitoring studies have confirmed that humans and the environment are exposed to a wide range of PFAS, with increasing ratios of unidentified ones.[25] For many of these compounds, there is little to no understanding on how much has been, and will be, released and transformed or accumulated into the environment and biota over time. A brief overview of PFAA detection in the abiotic and biotic environment is summarized below.

1.1.2.1 Abiotic Environment

Through their widespread use and long-range transport potential, PFAAs are widely distributed in the global environment and are commonly found in remote regions such as the High Arctic. Many studies have monitored and measured PFAAs in air, precipitation, ice caps, and the terrestrial, freshwater and marine environments, with both short-term and long-term records (Tables 1.3-1.4).

Atmospheric PFAAs as well as neutral precursors have been measured at long-term air-monitoring sites, predominantly in the northern hemisphere,[26–28] during ship

cruises along the Northern Atlantic Ocean and Canadian Archipelago,[29,30] and in some industrialized and urban areas.[31] Most PFAAs are measured in the particulate phase, while neutral precursors are measured in both gas and particulate phase.[32] Measurements of these PFAAs are usually on the order of a few pg m^{-3}, with concentrations in populated areas higher than those in remote areas. Similar trends in atmospheric measurements have been found in precipitation. PFAAs in precipitation are the result of wet deposition of PFAAs in particles and the gas phase, with levels ranging from hundreds of pg L^{-1} to a few ng L^{-1}. Both short- and long-chain PFCAs and PFSAs have been measured in various types of precipitation samples worldwide, comprising rainwater, snow and ice. Many studies have investigated concentrations of PFAAs in ice/snow cores and surface snow in the Arctic.[33–38] The high detection of these compounds in the remote Arctic environment is evidence of atmospheric and oceanic transport. Wet precipitation samples have been collected in several remote, rural and urban areas in North America, Europe and Asia.[39–41]

Freshwater is the dominant abiotic medium sampled for PFAAs. Due to the relatively small volume of most freshwater bodies, concentration effects facilitate the detection of PFAAs with concentrations ranging from hundreds of pg L^{-1} up to tens of μg L^{-1}. Point sources, such as AFFF release, have known to increase PFAA concentrations in downstream receiving bodies.[42] A wide range of PFAAs have been detected in North American lakes including The Great Lakes[43,44] and Canadian Arctic lakes.[27,45] Similarly, PFAAs have been measured in river and surface water samples in areas such as Norway,[38] Switzerland,[46] China,[47] and Japan.[48]

PFAAs are also globally distributed in the marine environment,[49] albeit at lower concentrations. The ocean is an important sink and transport pathway for these compounds. Concentrations of PFAAs in seawater typically range from a few to hundreds of pg L^{-1}. Spatial trends in PFAA contamination have been observed, where higher concentrations are detected near polluted coastal regions and lower concentrations in remote ocean waters.[11] Many inflowing rivers are sources of PFAA contamination, with major rivers in Europe and North America delivering tonnes of PFAAs per year into the Atlantic Ocean and surrounding seas.[50] Concentrations of PFAAs are also elevated in surface ocean waters where ice melting occurs.[51] Additionally, there is a latitudinal gradient, where concentrations of PFOA, PFOS, and other PFCAs, are greater overall in the northern hemisphere than in the southern hemisphere.[52,53] This is consistent with the location of most fluorochemical manufacturers and consumers in the northern hemisphere.

There is limited data on PFAA concentrations in the terrestrial environment compared to freshwater and marine environments. Based on available data, the PFCA composition differs among types of vegetation. PFOA is the predominant PFCA in plants, while the longer chain PFCAs are predominant in lichen and moss,[54] however further research is warranted to establish the consistency of these trends (Tables 1.5-1.6).

1.1.2.2 Biotic Detection

Many studies have detected and monitored PFAAs at all levels of the food web, in different aquatic and terrestrial species and in humans (Tables 1.5-1.6). However, due to

the complex and widespread distribution of these PFAAs, the relative contribution to source exposure is difficult to assess. PFAAs have been reported in organisms at all levels of the aquatic food web. They have been measured in plankton, benthic algae and various invertebrates from different regions across North America, Europe and Asia.[6,45,49,55,56] PFOS is the dominant PFAA detected in aquatic invertebrates, in addition to fish.[57] Elevated PFOS concentrations have been found in liver, muscle and egg samples of various fish species from different locations.[58] Other long-chain PFAAs, including PFOA, will bioaccumulate in the marine food web, particularly in fish, with greater bioaccumulation with increasing chain length.[55,59,60] Many PFCAs and PFSAs have been detected in both fresh and salt water fish samples from numerous regions.[6,44,45,55,61,62] Elevated levels of PFOS have also been reported in turtles and frogs from areas in the United States (U.S.).[6]

In general, the highest PFAA concentrations have been found in organisms at higher trophic levels, such as predatory birds and marine mammals.[61] Numerous PFAAs have been detected worldwide in seabirds, waterfowl and terrestrial birds,[6,61,63,64] although most studies have focused on PFOS and PFOA.[58] Fish-eating birds have higher PFAA concentrations than birds that are herbivores or insectivores, but lower concentrations than fish-eating mammals. This is likely linked to their trophic position in the food web or to a shorter elimination half-life.[58] PFAAs have been detected in Arctic fox and mink at comparable concentrations to those in marine mammals,[64] including polar bears,[64] seals,[65] whales,[66] and dolphins.[67] The highest PFAA concentrations have been found in bottlenose

dolphins from the U.S. and in polar bears from the Arctic, who are top predators in the Arctic food web.[58]

PFAAs have been detected globally in human blood and serum, with PFOS and PFOA most prevalent.[4] Overall, higher concentrations of PFOS have been measured in the blood and serum of North Americans compared to people in other parts of the world.[58] Comparing PFAA contamination between humans and wildlife, different patterns are observed, suggesting fish and mammals are not major sources of PFAA contamination to most humans (exceptions would be populations subsisting on marine mammals such as Northern indigenous groups). Rather, human exposure to PFAAs can occur through a variety of pathways, including exposure from personal care and cleaning products, intake of drinking water and food, inhalation of indoor and outdoor dust, and exposure during gestation.[68] The most prevalent PFAAs are readily detected in the plasma of pregnant women, in cord blood, and in neonatal blood spots.[69] Exposure can also occur during the postnatal period. A longer duration of breastfeeding during infancy increases exposure of PFAAs and resulting blood levels, as do dietary sources in childhood and adulthood.[69] Young children may have a higher uptake of PFAAs than adults due to more hand-to-mouth contact and exposure to dust on household surfaces, and greater food consumption relative to body weight.[70] PFAAs have been detected in food-packaging[71] and in food composites,[57] both potential sources of direct exposure.[72] Consumption of drinking water is another route of exposure, with numerous studies detecting PFAAs in various drinking water sources in different countries.[57,73,74] Human PFAA exposure from drinking water is a serious concern because of the high aqueous solubility of these compounds. Elevated

PFAA concentrations in U.S. drinking water have been reported in numerous regions, especially near industrial sites that produce or use them.[73] Many airports and military fire training areas are contaminated by PFAAs contained in AFFFs, used during firefighting training activities. Groundwater and surface waters surrounding these sites have been reported with concentrations 3 – 4 orders of magnitude higher than the United States Environmental Protection Agency (US EPA) health advisory level for drinking water.[75] Wastewater treatment plants (WWTPs) are important PFAA sources because these compounds are not removed by standard wastewater and drinking water treatment processes and precursor compounds biodegrade, which increases the concentrations of PFAAs in effluent relative to influent.[76,77] Land application of the biosolids generated by WWTPs may then contribute to human exposure through subsequent contamination of water, food, livestock, and wildlife[75] (Tables 1.3-1.4). Indoor and outdoor dust are also potential sources of human exposure, through inhalation of airborne material and hand to mouth contact, with very high concentrations of PFAAs detected in house dust[78] and outdoor dust.[79]

Table 1.3. PFCA concentrations (ng L^{-1}) in selected abiotic samples. Air sample concentrations are in pg m^{-3}. When analytes were not part of the monitored suite, cells are left empty.

Matrix	Site	TFA	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Air (gas/particle) (2006)	Albany, New York[31] (pg m^{-3})						<0.12-0.81	0.76-6.53	<0.12-0.40	0.13-1.56	<0.12-0.16	<0.12-0.38
Air (particulate) (2005-2006)	Europe (UK, Ireland, Norway)[28] (pg m^{-3})					0.5-107	<0.001-14.4	8.9-552	0.2-26.6	<0.15-8.3	<0.002-4.6	<0.12
Ice Core (1996-2005, 1995-2008)	Devon Ice Cap, Canadian Arctic[33,34]			0.258-2.62	0.06-0.693	0.052-0.604	0.219-1.05	0.034-1.02	0.005-2.27	0.004-0.369	0.003-0.376	0.002-0.041
Snow Core (1996-2008)	Colle Gnifetti, Swiss Alps[35]			0.34-1.83	<0.03-0.40	0.06-0.34	0.04-0.22	0.20-0.63	<0.12-0.31	<0.06-0.24	<0.10-0.18	
Snow Core (1980-1999, 1996-2007)	Mt. Muztagata, Mt. Zuoqiupu, Tibetan Plateau[36]			<0.013-0.056	<0.025-0.142	<0.02-0.10	<0.02	0.038-0.243	<0.01-0.073	0.008-0.075	<0.005-0.011	<0.01-0.033
Surface Snow (2004)	Greenland[37]					<0.01-0.035	0.012-0.085	0.051-0.52	<0.03-0.077	0.11-0.149		
Surface Snow (2006)	Longyearbreen Glacier, Longyearbyen, Norway[38]			0.109 ± 0.045	0.030 ± 0.004	0.076 ± 0.04	0.017 ± 0.006	0.113 ± 0.02	0.051 ± 0.009	0.022 ± 0.004	<0.005	0.007
Precipitation (1998-1999)	Rural U.S. (Ithaca, New York)[39]	3.0-360	<0.10-21	<0.10-4.60	<0.10-17	<0.10-10	<0.10-11	<0.10-10	<0.10-3.20			
Precipitation (2002)	Remote Canada (Kejimkujik, Nova Scotia)[39]	4.0-100	<0.10-59	<0.10-2.90	<0.10-1.90	<0.10-2.30	<0.10-5.40	<0.10-3.10	<0.10-3.30			
Precipitation (2003-2004)	Urban Canada (Toronto, Ontario)[39]	87-270	0.80-2.40	0.10-2.10	0.20-1.10	0.20-0.90	<0.10-1.70	1.0-11	0.50-9.70	<0.07-1.0	<0.07-3.70	<0.07-5.20
Precipitation (2007, 2008)	Japan (Tsukuba & Kawaguchi) [40, 41]	52.4-69.8	0.90-45	<0.05-17.3	<0.05-4.97	<0.25-4.21	0.15-3.97	0.11-11	0.16-17.5	0.04-2.11	0.06-2.06	<0.05-0.62
Precipitation (2007)	U.S.A. (Slingerlands & Downtown Albany)[41]		1.08-20.3	<0.005-1.01	<0.05-2.24	<0.25-1.11	0.17-1.13	0.25-9.42	0.21-5.39	0.10-0.42	<0.25-1.91	<0.05-0.13
Precipitation (2007)	China (Hong Kong)[41]		1.13-3.08	0.53-1.79	<0.05-0.23	<0.25-0.62	<0.25-15.7	0.20-0.41	0.13-0.44	0.14-0.31	0.04-0.19	0.06-0.16

Table 1.3. PFCA concentrations (ng L^{-1}) in selected abiotic samples continued.

Matrix	Site	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Lake Water (2004-2010)	The Great Lakes[44]		0.16-4.95	0.329-4.64	0.12-2.39	0.244-7.16	0.047-0.642	0.005-0.958	0.004-0.026	0.005-0.01
Lake Water (2003-2005)	Canadian Arctic Lakes[27]				0.30-49	0.40-16	0.20-6.10	0.50-29	0.20-5.90	0.50-2.30
Surface Water (2009)	Shenyang, China[47]			1.26-37.6	0.56-4.00	1.83-10.9	<0.39-1.60	<0.33-0.66	<0.28-1.20	<0.30-2.48
River Water (2008)	Kansai, Japan[48]		0.10-0.80	0.10-1630	0.30-5.00	2.70-500	1.50-902	0.10-7.20	0.20-17.5	
River Water (2009)	Switzerland[46]	<0.069-7.04	<0.041-13.5	0.071-15.5	0.028-3.07	0.036-30.3	<0.028-30	<0.010-5.05	<0.034-2.56	<0.051-0.303
Lake Sediment (2003-2005)	Canadian Arctic Lakes[27]				<0.18-6.80	<0.290-7.50	<0.059-3.20	<0.059-0.60	<0.46	<0.55
Ocean Water (2005, 2008)	Arctic Ocean[50]			0.003-0.065	0.011-0.084	0.007-0.054	0.003-0.047	0.002-0.033	0.0009-0.079	0.001-0.032
Ocean Water (2010)	Arctic Ocean[51]	<0.13-0.36	0.031-0.24	<0.027-0.028	<0.011-0.24	<0.020-0.067	<0.022-0.051	<0.035	<0.021-0.024	<0.009
Ocean Water (2007, 2009)	Atlantic Ocean[50]			0.003-0.15	0.002-0.11	0.003-0.26	0.002-0.13	0.003-0.03	0.0001-0.092	0.0002-0.094
Ocean Water (2008)	Atlantic Ocean[52]	<0.15-0.496	<0.014-0.097	<0.003-0.117	<0.003-0.037	<0.005-0.223	<0.003-0.039	<0.006-0.037	<0.011-0.066	<0.006-0.048
Ocean Water (2011)	Atlantic, Pacific, & Indian Oceans[49]			0.0008-0.20	0.003-0.080	0.013-0.10	0.0002-0.48	0.003-1.60		
Drinking Water (2013-2015)	United States (UCMR3 Data)[73]				10-22	20-53				
Drinking Water (2007)	Catalonia, Spain[74]			<0.87	<0.61-3.02	0.32-6.28	0.22-0.52	<0.82	<0.43	<0.34
WWTP Effluent (2014)	San Francisco Bay[76]	16 ± 5.80	12 ± 11	26 ± 5.10	4.40 ± 2.20	21 ± 13	8.40 ± 3.60	3.50 ± 1.70		
Influent/Effluent (2010)	20 Canadian WWTPs[77]	<1.00-89.0	0.50-192	0.70-258	1.08-74.6	<1.04-138	<0.986-18.2	<0.98-11.6	<1.07	<1.2

Table 1.4. PFSA concentrations (ng L^{-1}) in selected abiotic samples. Air sample concentrations in pg m^{-3}.

Matrix	Site	PFBS	PFHxS	PFHpS	PFOS	PFDS	FOSA
Air (gas/particle) (2006)	Albany, New York[31] (pg m^{-3})		<0.12-0.44		0.35-3.0	<0.12-0.18	
Air (particulate) (2005-2006)	Europe (UK, Ireland, Norway)[28] (pg m^{-3})	<0.09-3.2	0.04-5.9		1.0-46	<0.001-0.8	<0.2-2.1
Ice Core (1996-2005, 1995-2008)	Devon Ice Cap, Canadian Arctic[33,34]				0.006-0.18		0.092-1.24
Ice Core (1992-2005)	Longyearbreen Glacier, Norway[38]				0.008 ± 0.002		
Snow Core (1980-1999, 1996-2007)	Mt. Muztagata, Mt. Zuoqiupu, Tibetan Plateau[36]				<0.025-0.346		
Surface Snow (2004)	Greenland[37]				0.025-0.137		0.024-0.039
Surface Snow (2006)	Longyearbreen Glacier, Norway[38]				0.034 ± 0.013		
Precipitation (2007, 2008)	Japan (Tsukuba & Kawaguchi) [40, 41]	<0.05-2.00	<0.05		<0.10-4.21		<0.05-0.25
Precipitation (2007)	U.S.A. (Slingerlands & Albany)[41]	<0.05-0.62	<0.05		<0.10-0.64		0.03-0.31
Precipitation (2007)	China (Hong Kong)[41]	<0.05-3.07	<0.05		<0.10-0.70		<0.05-0.22
Lake Water (2004-2010)	The Great Lakes[44]	0.011-1.80	0.027-1.56		0.095-9.48		
Lake Water (2003-2005)	Canadian Arctic Lakes[27]		1.50-24		0.90-90	1.00-14	
Surface Water (2009)	Shenyang, China[47]		<0.75-1.50		<0.20-3.32		
River Water (2008)	Kansai, Japan[48]	0.10-4.90	0.20-18.4		0.30-104		
River Water (2009)	Switzerland[46]	<0.015-9.99	0.033-14.8		<0.038-139		
Lake Sediment (2003-2005)	Canadian Arctic Lakes[27]	<1.1	<0.55-3.50		<0.35-85	<0.53	
Ocean Water (2005, 2008)	Arctic Ocean[50]		0.0007-0.019		0.009-0.039		0.001-0.044
Ocean Water (2010)	Arctic Ocean[51]	<0.017-0.078	<0.066	<0.019	<0.021-0.053	<0.006-0.01	<0.081-0.26
Ocean Water (2007, 2009)	Atlantic Ocean[50]	0.002-0.22	0.001-0.051		0.013-0.19		0.0005-0.046
Ocean Water (2008)	Atlantic Ocean[52]	<0.004-0.05	<0.004-0.053		<0.011-0.232		<0.003-0.067
Ocean Water (2011)	Atlantic, Pacific & Indian Oceans[49]	0.004-0.29	0.003-0.87	0.002-0.20	0.034-5.00		
Drinking Water (2013-2015)	United States (UCMR3 Data)[73]		32-120		41-156		
Drinking Water (2007)	Catalonia, Spain[74]	<0.27	<0.18-0.28		0.39-0.87		<0.19
WWTP Effluent (2014)	San Francisco Bay[76]	2.70 ± 1.50	4.80 ± 0.90		13 ± 4.40		
Influent/Effluent (2010)	20 Canadian WWTPs[77]	1.61-69.2	1.48-453		<2.01-1237		<0.972-86

Table 1.5. PFCA concentrations (w/w) (ng g^{-1}) in selected biotic samples.

Matrix	Site	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
Vegetation (2008-2009)	Canadian Territories[54]					<0.004-0.7	<0.004-0.228	<0.004-0.38	<0.004-0.121	<0.004-0.8	<0.004-0.092	
Plankton (2011)	Atlantic, Pacific, Indian Ocean[49]	0.1-7.6	0.5-8.2	0.1	0.6-9.1	0.5-6.7		0.1-0.5	0.1-1.7	0.2	0.1	0.2
Invertebrates (Benthic & Pelagic) (2010-2011)	6 Canadian Arctic Lakes[45]			0.017-0.38			0.01-9.8	0.13-2.0	0.21-2.42			
Invertebrates/Fish (2001)	Lake Ontario[55]					1.0-90	0.8-57	1.3-32	1.3-41	1.8-14	1.5-15	<0.5-7.3
Seafood Soft Tissue (2004)	China (Guangzhou, Zhoushan)[56]			<0.25-0.29	<0.25-0.41	<0.25-1.67	<0.25-0.61	<0.25-0.30	<0.25-0.77			
Char (Juvenile & Adult) (2010-2011)	6 Canadian Arctic Lakes[45]			0.001-0.058		0.10-50.6	0.11-6.2	0.023-0.84	0.04-0.50			
Herring (liver) (1980-2014)	Swedish Coast (Gulf of Bothnia, Baltic Proper)[61]					0.212-3.95	0.141-5.09	0.071-1.93	0.071-2.32	0.057-0.81	0.035-1.16	
Lake Trout (2006)	Great Lakes (Lake Superior)[44]					<0.42	0.70 ± 0.12	0.39 ± 0.07	1.1 ± 0.30	0.38 ± 0.08	0.97 ± 0.26	0.21 ± 0.05
Lake Trout (2001)	5 Great lakes[62]				<0.02-1.43	1.1-4.4	0.57-2.9	0.72-4.9	0.74-3.5	0.37-0.97	1.1-3.5	0.72-1.8
Glaucous Gull Plasma (2004)	Norwegian Arctic[63]					<0.70-0.74	<2.33-6.33	3.07-15.1	32-184	2.9-23.9	3.63-30.2	<0.25-2.77
Eggs (White-Tailed Sea Eagles) (1966-2010)	Sweden (Gulf of Bothnia, Baltic Proper, Lapland)[61]					0.072-2.23	0.059-47.1	0.015-40.9	0.036-49.6	0.019-11	0.112-45.9	0.021-4.11
Arctic Species (polar bear, seal, fox, mink, loon, fulmar, fish) (1993-2002)	Canadian Arctic (QC, NU, NWT, YK)[64]			<2.0-8.6	<0.5-80	<0.5-56	<0.5-63	<0.5-6.2	<0.5-11	<0.5-1.7	0.53-3.5	<0.02-0.84
Pilot Whale muscle (1986-2013)	Faroe Islands[66]					<0.006-0.14	<0.01-0.03	0.06-0.17	<006-0.51	<0.01-0.73	0.5-2.0	0.19-0.46
Ringed Seal Liver (1972-2005)	Nunavut, Canada[65]				<1.6	<0.85-6.2	0.15-12	0.14-10.2	0.20-36	0.17-5.8	0.11-8.1	0.01-1.05
Bottlenose Dolphin Blood (2003)	Western Atlantic Ocean, Gulf of Mexico[67]					0.6-163	3.0-547	4.3-542	1.7-343	<0.5-62	<0.5-37	<0.5-4.0
Human Blood Serum (1998-2004)	U.S., Columbia, Brazil, Italy, Poland, Belgium, India, Malaysia, Korea, Japan[4]					<1-256						
Maternal Human Blood Plasma (1999-2000)	Massachusetts, U.S.[70]					0.90-20.5	<0.1-3.4	<0.1-1.0				
Child Blood Plasma (2007-2010)	Massachusetts, U.S.[70]					<0.1-14.3	<0.1-25.7	<0.1-1.9				
Outdoor Dust (2013)	Mainland China[79]	0.97-20	8.0-12	0.3-7.1	0.35-26	0.2-100	0.11-5.1	0.17-11	0.03-3.4	0.03-8.8		
House Dust (2000-2001)	North Carolina & Ohio, U.S.[78]			54.2-1250	50.2-1150	142-1960	<11.3-263	<9.4-267	<10.7-588	<11-520		

Table 1.6. PFSA concentrations (w/w) (ng g^{-1}) in selected biotic samples.

Matrix	Site	PFHxS	PFOS	PFDS	FOSA
Vegetation (2008-2009)	Canadian Territories[54]		<0.003-0.231		
Plankton (2011)	Atlantic, Pacific & Indian Oceans[49]	0.1-0.9	0.1-43	0.1-0.2	
Benthic Organisms (1998-1999)	Rivers in Michigan and Indiana, U.S.[6]	<2	<2-41.3		<1-6.3
Invertebrates (Benthic & Pelagic) (2010-2011)	Six Canadian Arctic Lakes[45]		0.12-445		0.01-0.75
Invertebrates/Fish (2001)	Lake Ontario[55]		13-450		4.0-180
Seafood Soft Tissue (fish, shrimp, mollusc, crab, shellfish) (2004)	China (Guangzhou, Zhoushan)[56]	<0.25-0.28	0.33-13.9		
Fish Tissue (1999-2000)	Michigan Waters, U.S.[6]	<34	64-263		<19
Char (Juvenile & Adult) (2010-2011)	Six Canadian Arctic Lakes[45]	0.18-2.0	<0.001-224		0.01-117
Herring (liver) (1980-2014)	Swedish Coast (Gulf of Bothnia, Baltic Proper)[61]	0.212-0.865	0.54-20.0		0.15-5.78
Lake Trout (2006)	Laurentian Great Lakes (Lake Superior)[44]	<0.10	2.3 ± 0.46	<0.10	
Lake Trout (2001)	5 Great lakes[62]	<0.01-6.2	4.8-121	0.69-9.8	0.25-2.1
Turtles, Minks, Frogs (1998-2001)	Michigan Watershed, U.S.[6]	<1-21	<35-18000		<1-103
Glaucous Gull Plasma (2004)	Norwegian Arctic[63]	0.29-2.71	48.1-349		
Bald Eagle Tissues (2000)	Michigan, U.S.[6]	<38	<7.5-1740		<75
Eggs (White-Tailed Sea Eagles) (1966-2010)	Sweden (Gulf of Bothnia, Baltic Proper, Lapland)[61]	0.111-5.02	6.912-1514	0.007-11.39	0.007-1.64
Arctic Species (polar bear, seal, fox, mink, loon, fulmar, guillemot, fish) (1993-2002)	Canadian Arctic (QC, NU, NWT, YK)[64]		1.3-3100		0.36-19
Pilot Whale muscle (1986-2013)	Faroe Islands[66]	0.11-0.19	2.0-4.0	<0.01-0.06	7.4-22
Ringed Seal Liver (1972-2005)	Nunavut, Canada[65]		0.58-177		0.03-3.62
Bottlenose Dolphin Blood (2003)	Western Atlantic Ocean, Gulf of Mexico[67]	2.2-332	46-3073		<0.5-102
Human Blood Serum (1998-2004)	Various Countries (U.S., Columbia, Brazil, Italy, Poland, Belgium, India, Malaysia, Korea, Japan)[4]	<0.4-32	<1-164		<0.4-26
Maternal Human Blood Plasma (1999-2000)	Massachusetts, U.S.[70]	<0.1-43.2	4.6-115		
Child Blood Plasma (2007-2010)	Massachusetts, U.S.[70]	<0.1-56.8	<0.1-51.4		<0.1-0.5
Outdoor Dust (2013)	Mainland China[79]		1.4-19		
House Dust (2000-2001)	North Carolina & Ohio, U.S.[78]	45.5-35700	201-12100		

1.2 Long-Range Transport

Long-range transport (LRT) refers to movement of pollutants over long distances. This section discusses the LRT potential of POPs and their precursor compounds, and the occurrence of these POPs in remote locations, such as the High Arctic, far from any sources. LRT implies that pollutants will move over political boundaries, necessitating that international regulations are critical. The LRT of POPs is therefore of political concern, with legislation, including the Aarhus Protocol and the Stockholm Convention, entering into force in the early 2000s.[80] Legislation initially regulated a set of 12 chemicals or groups of chemicals known as the 'dirty dozen'. Since then, additional pollutants have been added including PFOS, one of the major PFAAs. The LRT mechanisms of POPs, in particular the PFAAs, are of interest due to their different properties and ubiquitous detection in remote environmental samples.

In general, traditional POPs, those included in the 'dirty dozen', are persistent and volatile enough that they will undergo long-range atmospheric transport. POPs will undergo global distillation or multi-hopping, in which these persistent chemicals are emitted in temperate regions and transported to Arctic regions, where they condense with varying effectiveness, deposit, and accumulate in the environment, far from point sources.[81] The rates of these processes and the degree to which these chemicals accumulate in the Polar Regions, is dependent on their physicochemical properties and the prevailing atmospheric and oceanic conditions.[82] The PFAAs are different in that they are involatile with appreciable water solubility, and are therefore not subject to long-

range atmospheric transport or this global distillation mechanism. Various PFAS precursors on the other hand are volatile or semi-volatile and can be transported to remote Arctic regions before subsequently oxidizing to the PFAAs.[68] This too will depend on their physicochemical properties in terms of lifetime, whereby some compounds are long-lived and therefore globally well mixed, depending on their level of reactivity in the atmosphere.[83] The PFAAs, rather, are transported to remote locations via two other mechanisms: i) direct transport by oceanic currents and formation of marine aerosols;[84] and ii) atmospheric oxidative transformations and subsequent wet and dry deposition of volatile and semi-volatile precursors.[12]

1.2.1 Direct versus Indirect Transport

With direct transport, PFAAs can be directly transported in their carboxylic or sulfonic acid form to remote locations. PFAAs are first directly introduced into the ocean through either source locations or other water bodies, or deposited into the ocean from indirect formation of precursors.[85] Once in the ocean, PFAAs can be transported long distances via oceanic currents,[86,87] with high concentrations detected in the Arctic Ocean.[50,88] They can also be transported to land through the formation of marine aerosols that act as substrates.[89] PFAAs are highly acidic, surface-active compounds,[90] and will partition strongly into the sea surface microlayer (SSML).[91] The SSML is rich in organic matter content, has a thickness between 1 – 1000 μm and forms at the ocean surface.[92] When wave action occurs, air bubbles are formed containing organic-rich particles from the SSML, which will break, wafting these marine aerosols containing PFAAs and sea salts, into the atmosphere.[34] The organic carbon fraction of these marine aerosols

increases with a decrease in particle size.[93] Therefore, there is a greater enrichment of organic carbon and potentially PFAAs in smaller size particles.[26] These marine aerosols can then wet or dry deposit to remote land locations.

With indirect transport, PFAAs are produced through atmospheric oxidative transformations of volatile and semi-volatile PFAS precursors in the atmosphere.[12] These indirect precursor sources fall under three general categories: i) fluoropolymer industry, including both fluorotelomer-based and POSF-based products;[94] ii) CFC-replacement compounds; and iii) anaesthetics. Within the fluoroploymer industry, there are a number of compounds that will degrade in the atmosphere to produce minor yields of the PFAAs.[95–98] These compounds include perfluorinated aldehydes (PFALs), FTALs, FTOs, FTOHs, FTIs, FTAcs, and NAFSAs/NAFSEs, which are POSF-based precursors. The CFC-replacement compounds include HCFCs, HFCs, HFEs and HFOs. Anaesthetics include halothane, desflurane and isoflurane. The CFC-replacement compounds and the anaesthetics contain precursors that produce short-chain PFCAs as either major or minor products.[12] These various precursors will all undergo oxidation in the gas phase to form the various PFAAs. The atmospheric lifetimes of these precursors are determined by their reactions with hydroxyl radicals. For example, FTOHs have an atmospheric lifetime of approximately 12 – 20 days with respect to hydroxyl radical reactions, depending on the hydroxyl radical concentrations in the atmosphere which can vary with both location and season.[99,100] This relatively short lifetime means that FTOHs will have an inhomogeneous spatial distribution, but can be transported downwind long distances from emission points. An air mass travelling at the global average wind speed of 4 m s^{-1} could cover up

to 7000 km in ~20 days,[99] confirming that the atmospheric lifetime of these precursors, in particular the FTOHs, are long enough that they can reach remote locations (e.g. the Arctic) by air transport, before subsequently oxidizing to the corresponding PFAAs and depositing via wet or dry deposition.

1.2.2 Precursor Compounds

This section will focus on precursor compounds including the fluorotelomer and related compounds. The compounds that will be discussed in this section include the PFALs, FTALs, FTOs, FTOHs, FTIs, FTAcs, NAFSAs, and NAFSEs (POSF-based precursors).

Perfluoroalkyl iodides (PFAIs; $C_nF_{2n+1}I$), along with FTIs ($C_nF_{2n+1}CH_2CH_2I$) are the two starting raw materials that lead to the family of fluorotelomer-based products.[1] The accepted nomenclature uses FT as a prefix to designate fluorotelomer. FTOs ($C_nF_{2n+1}CH=CH_2$) are synthesized by dehydrohalogenation of FTIs or as an impurity from the synthesis of FTOHs from FTIs.[94] FTOHs ($C_nF_{2n+1}CH_2CH_2OH$) are key raw materials in the production of FTAcs ($C_nF_{2n+1}CH_2CH_2OC(O)CH=CH_2$). Perfluoroalkane sulfonyl fluorides (PASFs; $C_nF_{2n+1}SO_2F$) are main precursors in the manufacture of both PFSAs and other compounds containing the perfluoroalkane sulfonamido group ($C_nF_{2n+1}SO_2N<$).[1] Their major conversion is to the commercial product and building block, NAFSA ($C_nF_{2n+1}SO_2NH(C_mH_{2m+1})$), followed by a reaction to give NAFSE ($C_nF_{2n+1}SO_2N(C_mH_{2m+1})CH_2CH_2OH$).[1] These intermediates are also principal building blocks for many fluorochemical products used in various applications. Overall, the above

mentioned compounds are all used as raw materials for surfactant and surface protection products.[1]

The atmospheric fate of many of these PFAA precursors has been investigated using smog chamber techniques.[101] The atmospheric oxidation of these precursors lead to the formation of PFAL as an intermediate precursor and the PFAAs as final products[12] (Figure 1.2).

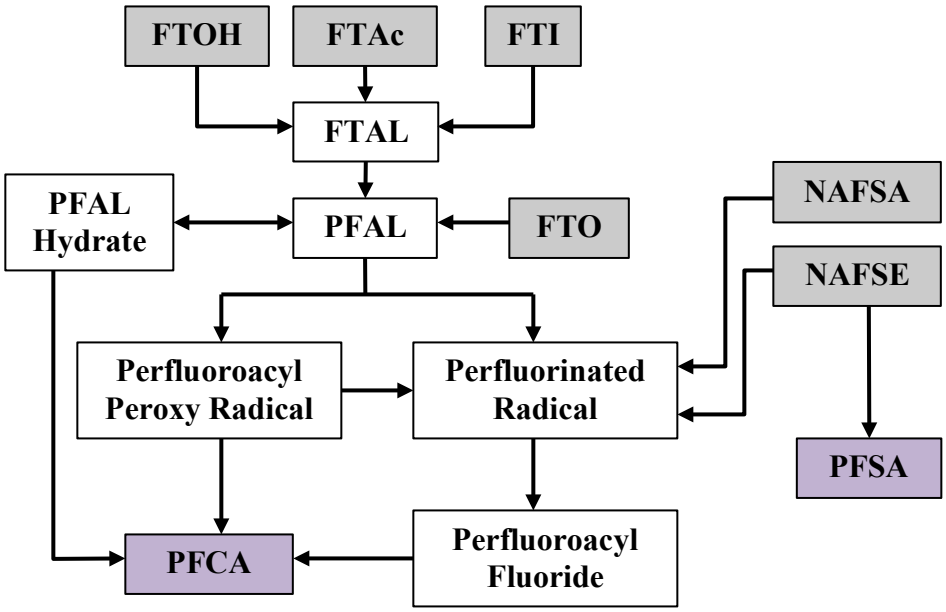


Figure 1.2. Atmospheric fate of volatile PFAA precursor compounds. Gray-shaded compounds are commercially produced. PFSA and PFCA are terminal products. Adapted from [12].

1.2.2.1 Atmospheric Chemistry of Precursor Compounds

The atmospheric lifetimes for many of the fluorotelomer species, including FTAL, FTOH, FTO, NAFSA, and NAFSE, are dominated by their reaction with hydroxyl radicals.[12] Atmospheric lifetimes of the PFALs and FTIs are limited by photolysis.[102]

Under most conditions, gas phase reactions are the primary degradation pathways of these above-mentioned precursors and their atmospheric lifetimes are expected to be on the order of days to weeks.[99] Table 1.7 summarizes the averaged measured rate constants with respect to hydroxyl radical reactions in the atmosphere and estimated atmospheric lifetimes for these precursor compounds. Numerous additional factors can impact the degradation rate, such as: seasonal changes of available light, anthropogenic pollution, and proximity to the coast or an anthropogenic chlorine source.[12] Conditions in the atmosphere will also influence product yield ratios, which depend on the available ratios of HO_2 and RO_2 to NO_x (NO_2 + NO).[103] These ratios vary depending on local conditions, such as urban versus remote conditions, with NO_x present at much greater mixing ratios near urban areas. Formation of PFAAs is more likely to occur in areas with low NO_x levels (i.e. remote locations such as the Arctic), where HO_2 and RO_2 are present at similar mixing ratios as NO_x.[103]

Table 1.7. Average measured hydroxyl radical rate constants and calculated atmospheric lifetimes (assuming constant [OH] of $1x10^6$ molecules cm^{-3}).

Precursor Compound	•OH Rate Constant (cm^3 $molecule^{-1}$ s^{-1})	•OH Average Lifetime (days)
PFAL Hydrate[104]	$1.22x10^{-13}$	90
PFAL[105]	$6.50x10^{-13}$	18
FTAL[100]	$29.6x10^{-13}$	4
FTOH[100]	$8.90x10^{-13}$	12
FTO[106]	$13.6x10^{-13}$	8.5
FTI[102]	$12.0x10^{-13}$	10
FTAc[107]	$113x10^{-13}$	1
NAFSA[108]	$3.74x10^{-13}$	35
NAFSE[96]	$58.0x10^{-13}$	2

Detailed mechanisms for the atmospheric reactions of each of these precursors with OH that form PFAAs have been elucidated, except for the formation of PFCAs from NAFSAs and NAFSEs[12] (Figure 1.2). The PFAL is the main precursor to the long-chain PFCAs (carbon chain lengths ≥ 4) and can be formed either from the FTAL or directly from FTOs, in the presence or absence of NO_x[12] (Figure 1.3). Other fluorotelomer compounds including FTOHs, FTAcs and FTIs will degrade in the atmosphere to form the FTAL as the primary product. These mechanisms are described elsewhere.[12]

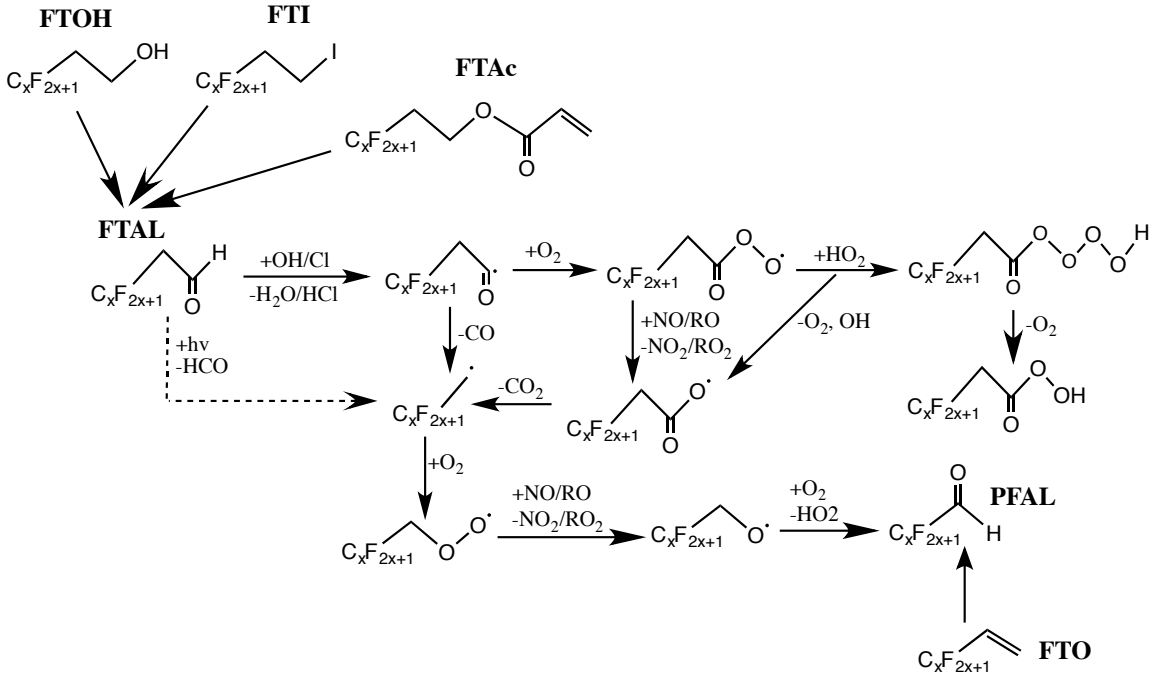


Figure 1.3. FTAL atmospheric oxidation mechanism. FTOH, FTI and FTAc form the FTAL through a number of oxidation steps. FTO will form the PFAL through a number of other steps. Data from [[12]] and references therein.

The PFAL, once formed from the reactions of other fluorotelomer precursors, will ultimately degrade to form the PFCAs via three different mechanisms (Figure 1.4). The first mechanism involves reaction of the PFAL hydrate with chlorine atoms or hydroxyl

radicals in the absence of NO_x to form the corresponding PFCAs.[104] This reaction will form trifluoroacetic acid (TFA) as the primary product in 100% yield.[12] The production of PFCAs from PFAL hydrates in the presence of NO_x has not yet been studied. The second mechanism involves reaction of perfluoro acyl peroxy radicals ($CF_3(CF_2)_xC(O)OO$) with HO_2 to form the PFCAs.[95] The perfluoro acyl peroxy radicals can also degrade by one of three channels, forming either PFCAs, perfluorinated peracids ($CF_3(CF_2)_xC(O)OOH$), or perfluorinated acyl oxy radicals ($CF_3(CF_2)_xC(O)O$).[109,110] The only perfluorinated peracid that has been detected is $CF_3C(O)OOH$.[110] The reaction with HO_2 leading to the formation of the PFCAs is most likely to occur in remote, low-NO_x environments.[111] The third mechanism involves the formation of perfluorinated radicals that will "unzip" to yield a carbon-equivalent number of molecules of carbonyl fluoride (COF_2) through reaction with NO.[95] Perfluorinated radicals can also react with peroxy radicals (R_2CHCOO), to form the corresponding PFCAs, in addition to the loss of hydrogen fluoride (HF).[95] The yield of PFCAs from fluorinated radicals will depend on the ratio of peroxy radicals to other reactive species, particularly NO_x.[97] FTOH degradation itself occurs on the order of weeks to months, therefore PFCA yields are highest in low-NO_x environments, i.e. remote locations.[112] Through the pathways illustrated in Figure 1.4, PFCAs of varying lengths will be formed. The biological fate of fluorotelomer-based compounds has been described in detail previously (e.g. Dinglasan et al., 2004[113] and Wang et al., 2005[114]) and will not be discussed here.

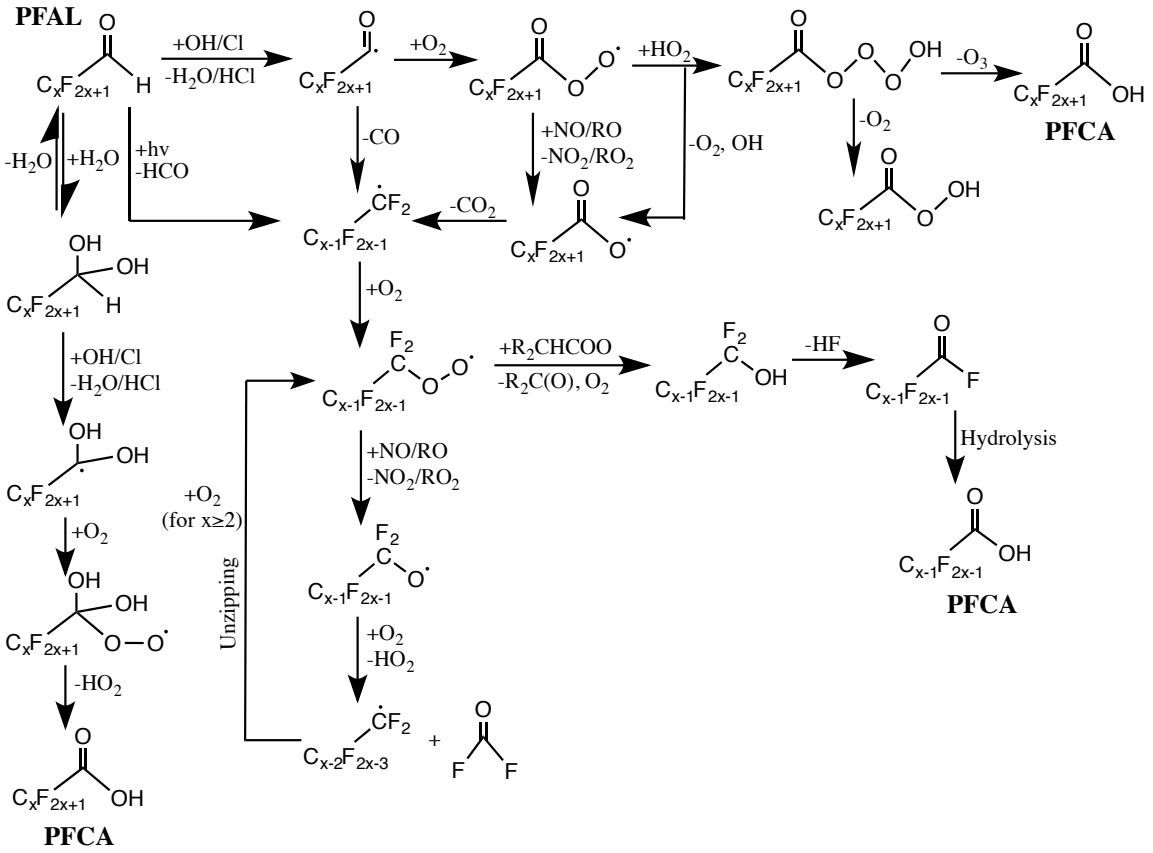


Figure 1.4. PFAL atmospheric oxidation pathway, with three different mechanisms for the formation of PFCAs. Data from [12,95,104,109,110].

1.2.2.2 Precursor Production Trends and Regulations

Figure 1.5 provides a general timeline of PFCA, PFSA and precursor production trends in terms of introduction and phase-outs, as well as PFAS regulations implemented up until recently. Between 1949 – 2002, PFCAs were directly produced using ECF by 3M, a global manufacturing company.[115] During this time they manufactured 80 – 90% of the ammonium perfluorooctanoate (APFO; PFOA-based product),[116] which was used as a processing aid in the manufacturing of fluoropolymers such as polytetrafluoroethylene (PTFE).[68] Major production sites of APFO during this time were in the United States and

Belgium and by 2002, there were 33 fluoropolymer manufacturing sites worldwide with the majority of them in North America, Japan, China and Europe.[94] From 1975 – 2004, the remaining 10 – 20% of APFO was manufactured by fluorotelomerization via direct oxidation of FTI, in Germany and Japan.[94] The total historical global production and emissions of APFO was estimated at 3.6 – 5.7 kt and 0.4 – 0.7 kt, respectively.[94] Thus, there are historic sources of directly synthesized PFOA by ECF and fluorotelomerization. Between 1975 – 2004, ammonium perfluorononanoate (APFN; PFNA-based product) was manufactured primarily in Japan[94] as a processing aid for polyvinylidene fluoride (PVDF) dispersion products.[117] APFN was manufactured by the oxidation of FTOs to the corresponding odd-numbered PFCAs, as well as by the FTI carboxylation process. The total historical global production and emissions of APFN was estimated at 0.8 – 2.3 kt and 0.07 – 0.2 kt, respectively.[94] From 1965 – 1975, PFCAs manufactured by ECF were used in AFFF,[94] but the major component of AFFF was PFOS. These AFFF formulations were used by the military, airports, and in oil/gas production, refining and industries. PFCAs and derivatives were also used as additives in industrial and consumer products from 1960 – 2000.[94] After 2002, 3M phased-out production of PFOA, and ECF manufacturing of APFO was replaced with the telomerization process.[116]

Between 1949 – 2002, 3M was also the major manufacturer of POSF using the ECF process.[118] They manufactured an estimated 65 kt of total global historic POSF from 1957 – 2002.[119] POSF-based products include diverse polymers and non-polymers in various industrial and consumer applications, where only the non-polymers readily degrade to PFOS.[120] POSF was also used in a series of reactions to produce N-methyl and

N-ethyl perfluorooctane sulfonamidoethanol (xFOSEs),[68] with total historic emissions of xFOSEs and PFOS estimated at 0.74 – 4.0 kt and 0.29 – 2.6 kt, respectively, from 1957 – 2002.[119] These xFOSEs were used in surface treatment and paper and board packaging applications. Commercial use of PFOS and its salts first started around 1970, and fluorotelomer-based products have also been manufactured since 1975 and used in many of the same consumer product and industrial applications as POSF-based products.[117]

Fluorotelomer-based raw materials and products are manufactured by a series of steps beginning with Telomer A, a basic raw material.[94] Other chemical reactions create fluorotelomer raw materials including fluorotelomer iodides, olefins, alcohols and acrylate monomers. FTOHs have been widely used in the production of polymers and surface coatings with an estimated production of 11 – 13 kt yr^{-1} in 2004.[68]

Starting in 2000, actions were taken by industry and regulators to reduce the release of PFCAs, PFSAs, and precursors, due to the environmental and health risks that many researchers discovered. Between 2000 – 2002, 3M voluntarily phased out production of POSF, PFOA and related products, including those based on C6, C8 and C10 chemistry.[121,122] They replaced this with products based on C4 chemistry, where compounds were derived from perfluorobutane sulfonyl fluoride (PBSF). This led to a decrease in POSF production by more than two orders of magnitude between 1998 and 2002.[123] During the phase out timeframe, a series of Significant New Use Rules (SNUR) were put in place in the U.S. to restrict production and use of materials that contained PFOS and its precursors.[124] By 2006, PFOS and related substances derived from POSF were regulated under the European Union (EU) Directive 2006/122/EC.[125] In 2006, the

US EPA worked with eight major fluoropolymer and fluorotelomer manufacturers to achieve the 2010/2015 PFOA Stewardship Program and reduce emissions and product content levels of PFOA, precursor compounds and related longer chain length homologues by 95% by 2010, and full elimination by 2015.[126] The same agreement was made in Canada as part of the Environmental Performance Agreement for that time.[127] In 2009, PFOS and related substances were listed under Annex B (restriction of production and use) of the Stockholm Convention on Persistent Organic Pollutants.[116] In 2012, long-chain PFCAs were categorized as potentially harmful pollutants in the Candidate List of Substances of Very High Concern (SVHC) for authorization under the REACH regulation.[128]

Since the early 2000s, there has been a geographical shift in PFAS production and emissions. Despite the phase-outs and regulations implemented by many major manufacturers in the United States, Western Europe and Japan, new manufacturers, largely in Continental Asia, have begun producing the long-chain PFCAs, PFSAs and their precursors. In China, PFOS production has increased rapidly since 2000 and PTFE production and PFOA use have increased ten-fold since the 1990s (60 kt of PTFE in 2015).[117] Between 2003 – 2008, China was reported to be the new main producer and user of PFOS substances, with <0.05 kt in 2003 and >0.25 kt of POSF-based products produced in 2008.[129]

As a result of the phase-outs, many alternative fluorinated products have been introduced and there has been a general transition to production of shorter chain PFAS that are believed to be less bioaccumulative and less toxic.[130] However, the short-chain

compounds are just as persistent and more mobile than their long-chain homologues[131] and most fluorinated products still contain highly complex, unpublicized mixtures with some still containing long-chain PFAS compounds.[122]

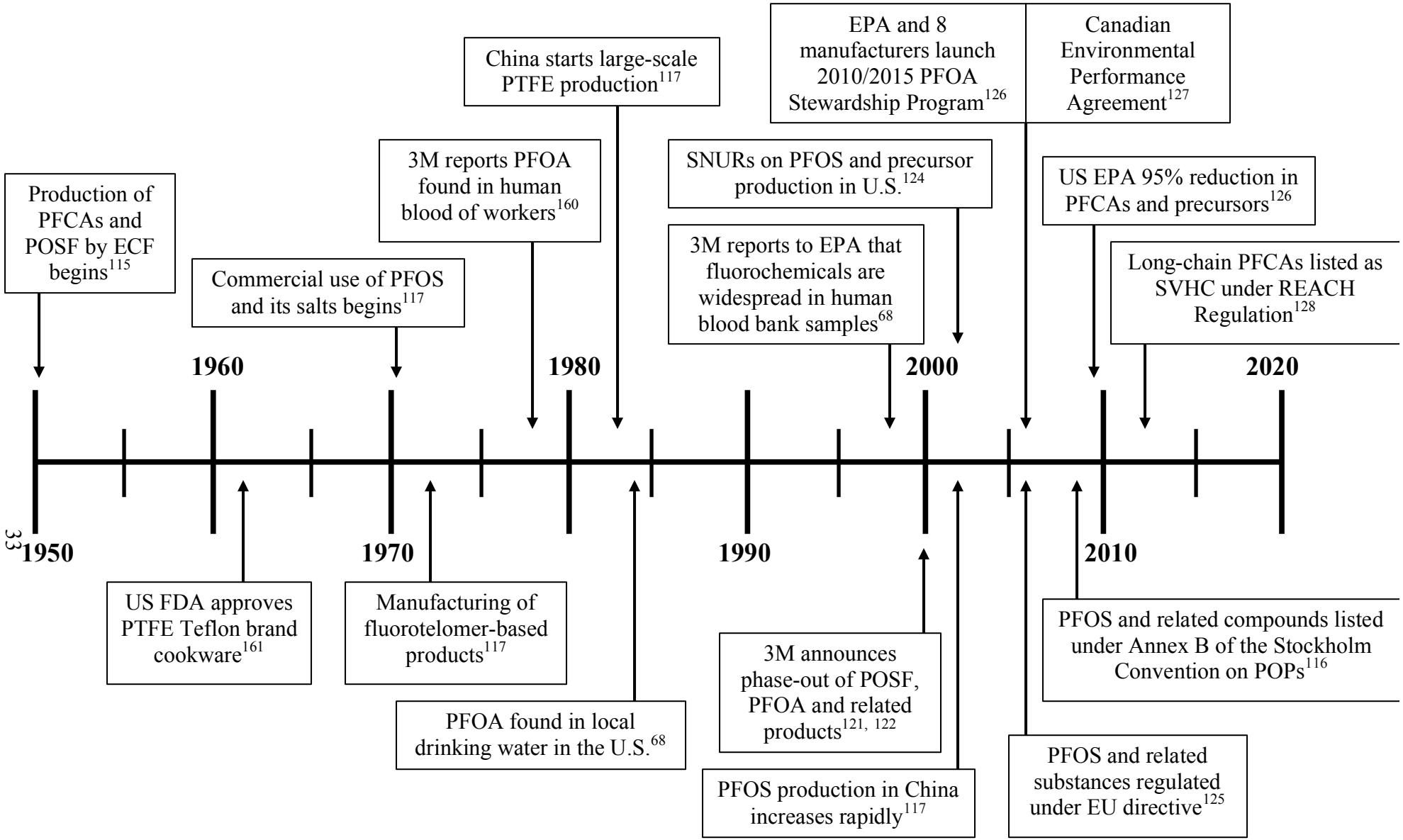


Figure 1.5. Timeline of PFAS production trends and regulations.

1.2.3 Chlorofluorocarbon-Replacement Compounds

This section will focus on the CFC-replacement compounds (HCFCs, HFCs, HFEs, HFOs) and anaesthetics that produce short-chain PFCAs as both major and minor degradation products. CFCs are chemicals that have been used extensively for industrial and domestic purposes since the late 1930s. They have physical properties that make them ideal for many uses but are also broken down by photolysis in the stratosphere, releasing chlorine (Cl) atoms that destroy ozone (O_3) molecules.[132] This in turn depletes the stratospheric ozone layer, leading to greater ground-level exposure to UV radiation. Mario J. Molina and F. Sherwood Rowland first discovered this in 1974,[133] which earned them the 1995 Nobel Prize in Chemistry, along with Paul J. Crutzen. Following this discovery, The Montreal Protocol on Substances that Deplete the Ozone Layer was signed in 1987 and entered into force in 1989, to regulate the production and consumption of these ozone-depleting substances (ODSs). The Montreal Protocol is a protocol to the Vienna Convention for the Protection of the Ozone Layer and is an international treaty, ratified by all 197 parties, designed to protect the ozone layer by mandating the phase out and replacement of ODSs including the CFCs, to reduce stratospheric ozone depletion.

HCFCs are CFC-replacement compounds used in a wide variety of applications. They are structurally similar to CFCs but contain a hydrogen atom that ultimately reduces the atmospheric lifetime of the molecule, resulting in reduced transport to the stratosphere and lower ozone depleting potential (ODP) compared to CFCs.[134] HCFCs that are major precursors to the short-chain PFCAs include HCFC-123, -124, -133a and -225ca. All of these precursors have been detected in remote air samples. HCFC-123 was first

commercialized in 1989 as a replacement for CFC-11 and has been used in refrigerants, centrifugal chillers and fire suppression agent blends.[135] It also has limited uses as a solvent and in foam blowing processes, and is used as an intermediate in the production of HFC-125. HCFC-124 began production in the early 1990s[136] and is used primarily in refrigerants, specialised air conditioning equipment, fire extinguishers and as a component of sterilant mixtures.[137] HCFC-133a has been detected in air samples since 1978, is an intermediate product in the syntheses of HFC-125, -134a and -143a, and is used for the production of pharmaceuticals, agrochemicals and the anaesthetic halothane.[138] HCFC-225ca was introduced as a replacement to CFCs in the early 1990s and is principally used in solvents.[132]

HFCs are CFC-replacement compounds commonly used in air conditioning and as refrigerants. They are structurally similar to HCFCs but do not contain any Cl atoms. HFCs have a very low ODP but are potent greenhouse gases. There are a number of major HFC precursors that produce short-chain PFCAs. HFC-134a, which began production around 1990, is one of the most prominent CFC-replacement compounds and is mainly used in mobile air conditioning as a substitute for CFC-12.[139] It is also used in domestic refrigeration,[140] some stationary air conditioners, in insulating foam production and in some HFC blends.[141] HFC-227ea emissions started in the mid-1980s through use in fire suppression, propellant, refrigerant, inhaler and foam blowing applications.[142] HFC-43-10mee was introduced in the mid-1990s as a cleaning solvent for the electronics industry, replacing other compounds including CFC-113, methyl chloroform, HCFC-141b and some perfluorinated compounds.[143] HFC-236ea is used as a replacement for

halons in fire suppression and as a refrigerant substitute.[144] It can produce HFC-245eb which is then used to produce HFO-1234yf.[145] There is little information on HFC-236cb, but it is structurally similar to the commonly used HFC-134a and is expected to be produced and released in small quantities.[146]

HFEs are CFC-replacement compounds that began development in the mid-1990s and were later introduced in 1996 as acceptable alternatives.[147] The HFEs that are major precursors to the short-chain PFCAs are also halogenated inhalation anaesthetics. HFE-236ea2 (desflurane) was introduced in 1992 for use in general anaesthesia. Isoflurane and halothane are two other anaesthetics that degrade to PFCAs, but were not part of The Montreal Protocol. HCFE-235ca2 (isoflurane), which is a hydrochlorofluoroether was introduced in 1981 to replace enflurane ($CFHClCF_2OCF_2H$).[148] Halothane (Halon-2311) was an early anaesthetic, mainly used in the 1960s and 1970s. It has since been replaced in developed countries due to its hepatotoxicity.[148]

HFOs are next generation CFC-replacement compounds, introduced in response to the ozone depletion and climate implications of CFC, HCFC, HFC, and HFE use. HFOs are structurally similar to HFCs with the inclusion of a double bond that decreases the atmospheric lifetime from years to days. A few HFOs are known short-chain PFCA precursors. HFO-1234yf (also called HFC-1234yf) is being developed as a next-generation mobile automobile air-conditioning refrigerant (MAC) to replace HFC-134a.[149,150] HFO-1234yf also has the potential for uses in other applications and is already being introduced as a propellant for aerosol products. HFO-1225ye(E) and -1225ye(Z) are two other HFO compounds, and have both been proposed as refrigerants.

1.2.3.1 Atmospheric Chemistry of CFC-Replacement Compounds

CFC-replacement compounds produce short-chain PFCAs as both major and minor products at yields ranging from <10% to 100%.[12] The lifetimes of these CFC-replacement compounds are generally dominated by gas phase hydroxyl radical reactions in the troposphere and the tropospheric lifetimes are summarized in Table 1.8.[12, 83]

The main degradation pathway for HCFCs, HFCs, HFEs and HFOs is hydroxyl radical reaction in the troposphere.[83] All of these compounds can also be degraded by reaction with Cl and NO_3 radicals, but not as main degradation pathways. These compounds can also transport to the upper atmosphere, but their atmospheric fates will be different.[83] This section focuses on the atmospheric chemistry of these CFC-replacement compounds in the troposphere only.

Table 1.8. Tropospheric lifetimes[12, 83] with respect to reaction with hydroxyl radicals[151] for CFC-replacement precursors.

Precursor Compound	Tropospheric Lifetime
HCFCs	1.2-6.0 years
HFCs	3.2-51 years
HFEs	0.1-10.8 years
HFOs	4.9-11 days

Mixed halides that are major precursors to the PFCAs include the HCFCs ($CF_3(CF_2)_nCHXY$), where X is fluorine, chlorine or hydrogen and Y is chlorine, and the HFCs (CF_3CFHX), where X is CF_3, CFH_2, CF_2H, or $CHFCF_2CF_3$. These compounds will undergo hydrogen atom abstraction followed by reaction with molecular oxygen and NO to yield an acyl radical.[12] The radical decomposes, eliminating the Y atom (in the case of

HCFCs) or X atom (in the case of HFCs), yielding a perfluoroacyl fluoride or chloride. This compound will readily hydrolyze to give the corresponding PFCA, usually TFA (Figures 1.6-1.7). The mechanism for HFC-134a (Figure 1.7) is similar to the mixed halide mechanism, but involves elimination of the H atom rather than a halide.[152] The atmospheric fate of volatile anaesthetics including halothane, isoflurane and desflurane, follow three slightly different mechanisms that all yield TFA.[12,153] Halothane follows the mixed halide mechanism illustrated in Figure 1.6. Isoflurane and desflurane, which both fall under the class of HFEs, will form alkoxy radicals that decompose and eventually hydrolyze to yield TFA,[153] as illustrated in Figure 1.8. Finally, HFOs ($CF_3CF=CXY$) where X and Y are either hydrogen and/or fluoride, will undergo atmospheric oxidation via the hydroxyl radical to produce a perfluoroacyl fluoride and subsequently, TFA,[12,154] as illustrated in Figure 1.9.

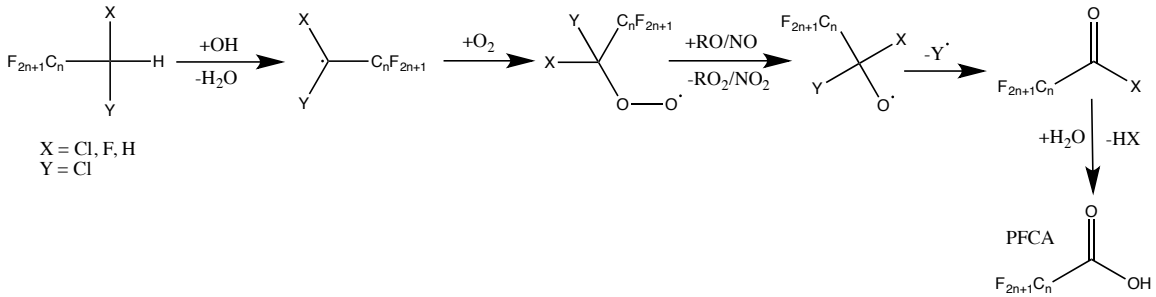


Figure 1.6. Mixed halide mechanism for HCFCs (HCFC-123, -124, -133a, -225ca) and halothane[12], where C_nF_{2n+1} has n=1 or 2 and X = Cl, F, H and Y = Cl.

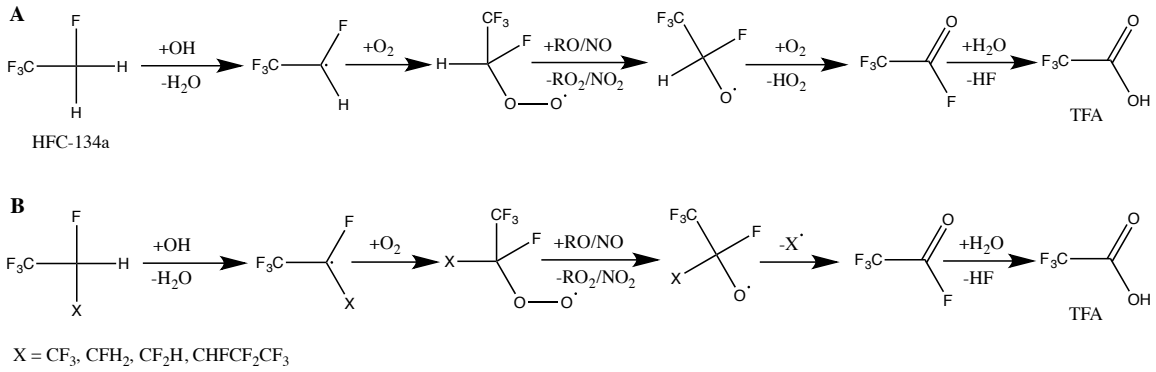


Figure 1.7. A) Degradation mechanism for HFC-134a to TFA[152]. B) Mixed halide mechanism for HFCs (HFC-227ea, -245eb, -236ea, -43-10mee)[12,83] (X = CF_3, CFH_2, CF_2H, or $CHFCF_2CF_3$).

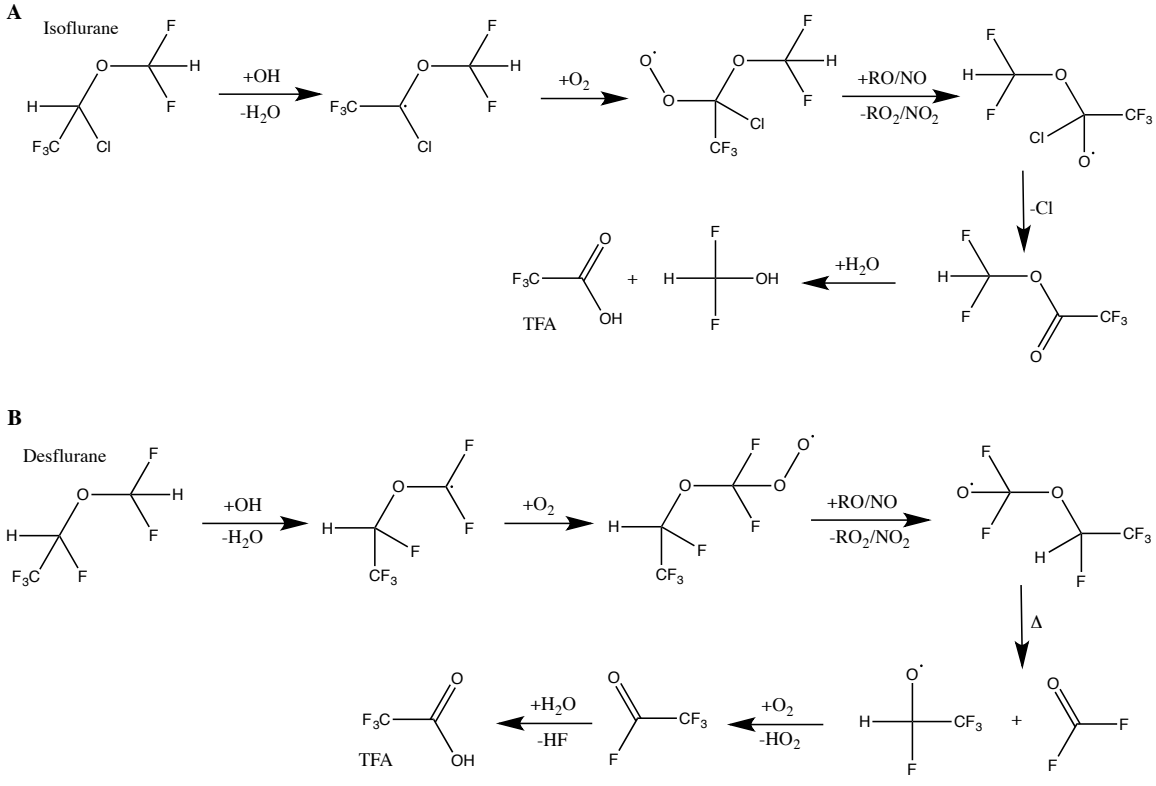


Figure 1.8. A) Degradation mechanism for isoflurane (HCFE-235da2) to TFA[12]. B) Degradation mechanism for desflurane (HFE-236ea2) to TFA[153].

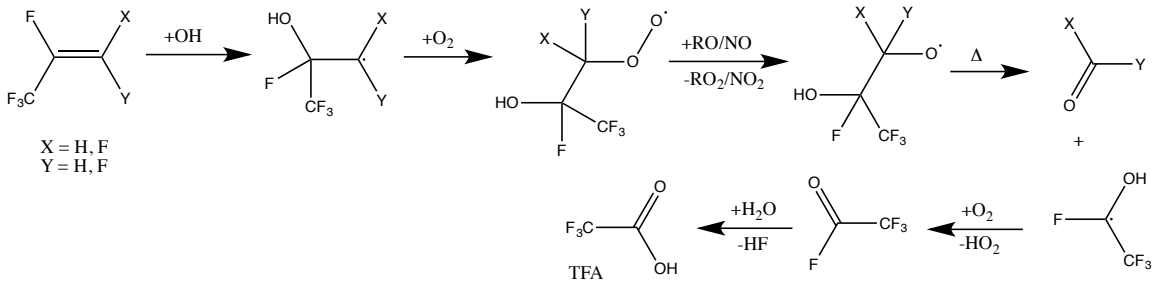


Figure 1.9. Mechanism for the atmospheric oxidation of HFOs (HFO-1234yf, HFO-1225ye (E)/(Z), PFO-1216) to TFA[12,154] (X = H, F and Y = H, F).

1.2.3.2 CFC-Replacement Production Trends and Regulations

Figure 1.10 outlines a general timeline of CFC-replacement compound production trends and regulations. CFCs were used extensively starting in the late 1930s until the 1974 discovery of their role in stratospheric ozone destruction.[133] They were subsequently labelled ODSs and regulated under The Montreal Protocol, which was implemented in 1989.[155] As a result of The Montreal Protocol, CFCs were phased out and quickly replaced with substitute compounds. These CFC-replacement compounds started being used on a large-scale around the 1990s. Halothane, an inhalation anaesthetic, was used mainly from 1960 – 1970.[148] Other anaesthetics including isoflurane and desflurane were introduced around 1981 and 1992, respectively.[148] From 1990 – 1999, a number of amendments were made to The Montreal Protocol to regulate HCFCs, with complete phase out by 2020 in developed countries and by 2030 in developing countries.[141] Emissions of HCFC-225ca began decreasing after 1999,[132] while emissions for other HCFC precursors began decreasing after 2003.[138,139] Production of HFCs has been increasing steadily since 1995 in developed countries, with China emerging as a major HFC producer and consumer in the early 2000s.[156] Emissions of HFC-134a have been

greatly increasing since the early 1990s[137] and HFC-43-10mee emissions began after 1995.[143] With the Kigali Amendment to the Montreal Protocol in 2016, a phasedown of HFCs has been proposed, with a freeze in 2024 and an 80% reduction by 2043 in developed countries, and a similar phase-out plan in developing countries.[155] HFOs are new CFC-replacement compounds, that are already being developed for use, with HFO-1234yf as the next-generation MAC refrigerant to replace HFC-134a.[149] Some of these HFOs have been introduced and production of HFO-1234yf in North America is already being estimated at 50 – 100 kt yr^{-1} in the next 50 – 100 years.[157]

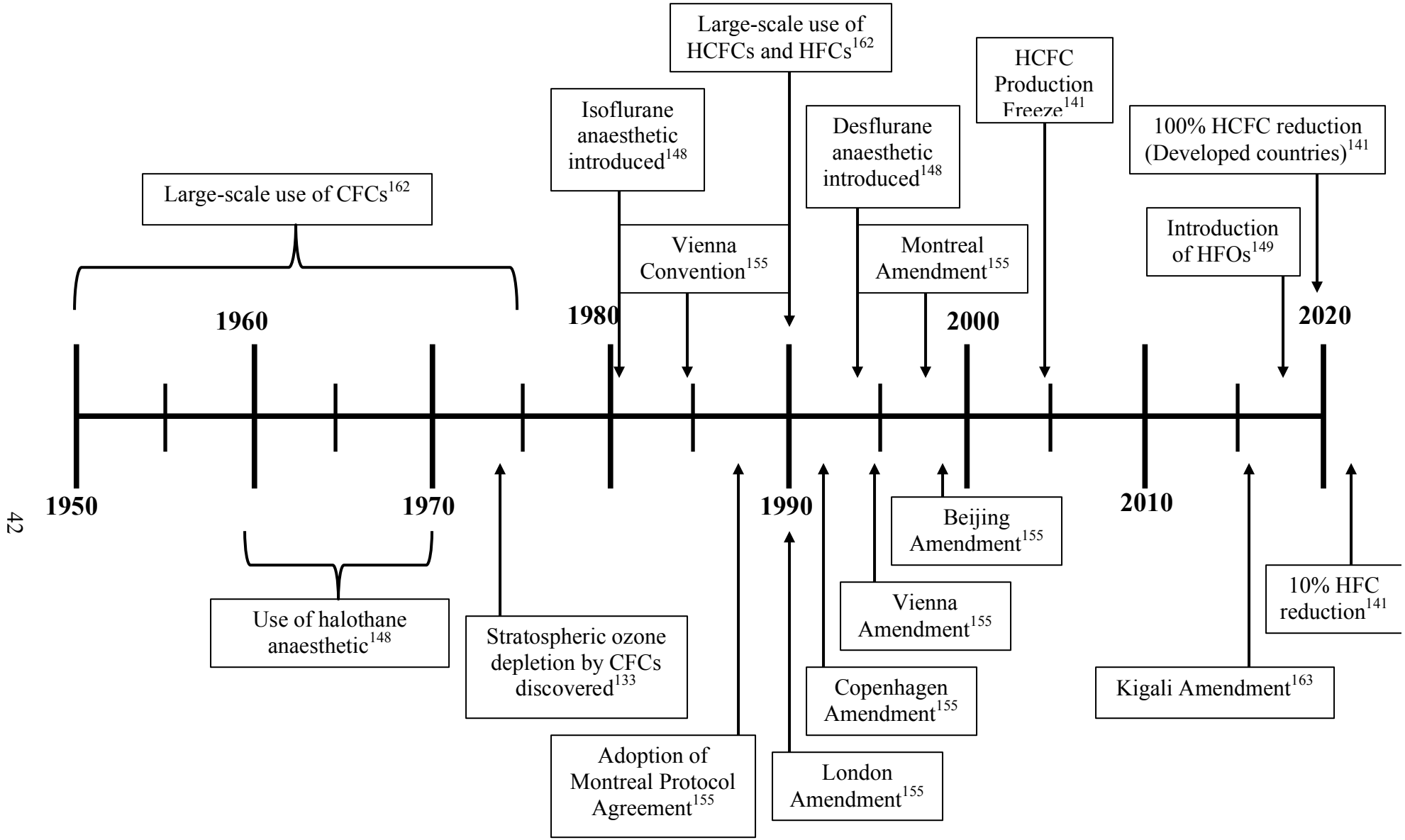


Figure 1.10. Timeline of CFC and CFC-replacement compound production trends and regulations.

1.3 Arctic Deposition and Sampling

The Arctic is a pristine environment, vulnerable to human impact. These impacts include increases in resources, fossil fuel uses, and industrial manufacturing that have led to releases of anthropogenic compounds into the environment.[158] Although remote, the Arctic is surrounded by populated continents that are releasing anthropogenic pollutants into the atmosphere and ocean. Following the industrial revolution, the Arctic has become very useful to researchers, as contaminants will persist in the Arctic for a long time and are effectively preserved and recorded in Artic ice and snow.[159] By analyzing ice cores and surface snow, these impacts can be evaluated and help us in understanding the mechanisms that govern the Arctic environment.

Ice cores provide an invaluable record of past atmospheric pollution by trapping and preserving this information in glaciers and ice caps following snow deposition.[158] As snow accumulates from year to year, a temporal record in contaminant deposition is created. These long-term archives provide useful data that helps researchers determine production changes, pollutant sources and transport pathways of contaminants over time. Ice core samples are typically collected using a mechanical or thermal drill and provide long-term records of pollution.[158] Snow pit samples are collected by digging a pit vertically into a snow pack and are used for short-term (due to depth restrictions via manual digging) reconstruction of pollution events. Remote arctic samples can be susceptible to contamination due to the trace analyses of pollutants in these samples and care must be taken at every step from sample collection to analysis.

Long-range transport mechanisms of PFAAs can be elucidated through the collection and analysis of ice core samples. High Arctic ice caps generally receive their contamination solely from atmospheric deposition due to their high elevation, and preserve a temporal record of that deposition. Various pollutants have been detected in remote Arctic environments and PFAAs themselves have been detected previously in ice cores, snow, and lake and ocean water, as summarized in Tables 1.3 and 1.4. Once collected, these ice cores can be sectioned and analyzed for PFAAs, and provide us with important information about their contamination and production changes over time and help us in understanding their transport mechanisms to the Arctic environment.

1.4 Thesis Objectives

This work aims to accomplish three main goals using an ice core collected from the Canadian Arctic: 1) examine a greater number of PFAA analytes, including the short-chain PFCAs, over a larger timescale compared to previous studies; 2) compare the temporal trends in PFAA deposition to production trends; and 3) further understand the long-range transport mechanisms of PFAAs and their precursors. This will be accomplished by extraction of a 15 m ice core and PFAA analysis by liquid-chromatography and ion-chromatography methods (Chapter 2); assessing the deposition, examining the temporal and homologue trends, correlating to production changes and previous measurements, and modelling to understand long-range transport (Chapters 3 & 4). Chapter 3 focuses on the long-chain PFCAs and the PFSAs, while Chapter 4 focuses on just the short-chain PFCAs.

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2 Methodology

2.1 Introduction

Perfluoroalkyl research in the Arctic presents many analytical challenges.[1] Firstly, Arctic fieldwork is logistically challenging, due to cost, environmental conditions, weather, remoteness, and requirement of specialized personnel. Analysis of ice cores requires instrumentation and infrastructure capable of ultra-trace level analysis. Due to the unique physicochemical properties of PFAS, and their ubiquitous presence in the environment, extracting and analyzing for these compounds from ice core samples in the laboratory presents a challenge. Extensive care must be taken and appropriate materials and techniques employed when doing PFAS extraction and analysis. Contamination and analyte loss at all stages of collection and analysis requires cognizance. Some PFAS preferentially sorb to glass from the aqueous phase, therefore use of glass is avoided wherever possible. PFAS also have many uses in common laboratory consumables, leading to numerous potential sources of contamination in the lab. HPLC systems typically contain internal fluoropolymer parts that cause contamination. Quantifying PFAS is ideally accomplished using accredited standards, but some PFAS are not commercially available, or their analogous isotopically labeled internal standards are not available. Structural isomers of PFAS, associated with ECF manufacture, are routinely encountered for certain analytes, many of which may have different instrument response compared to the n-isomer standards. This chapter describes the method for the ultra-trace detection of PFAS in Arctic ice core samples.

2.2 Ice Core Collection and Dating

The ice core collection and dating was carried out by specialized personnel outlined in the co-authorship statement, prior to the start date of my Master's program. This section will therefore provide just a brief overview of the collection and dating process that took place for understanding purposes. A 15.5 m ice core was collected from the summit of Devon Ice Cap, Devon Island, Nunavut (75.2° N, 82.7° W, 2175 m above mean sea level (AMSL)) on May 17, 2015. Samples were collected using a stainless steel Kovacs ice drill with a 9 cm diameter. Dating of the Devon Ice Cap ice core was completed using the oxygen isotope record and other glaciochemical records measured in a replicate core drilled at the same location. Oxygen isotope analyses were run on a Picarro cavity ring-down spectroscopy analyzer (precision for $\delta^{18}O$ of water samples is $\leq$ 0.1%). Sample isotope ratios were standardized using three working standards calibrated against the International Atomic Energy Agency (IAEA) standards VSMOW and SLAP. Final $\delta^{18}O$ values are on the VSMOW/SLAP scale. The $\delta^{18}O$ time series was used to establish an age-depth relationship by matching the $\delta^{18}O$ core record with local summer and winter solstice dates (linearly interpolating between solstices) (e.g., Criscitiello et al., 2014).[2] Elemental, ion, and H_2O_2 analyses were performed on an ICP-MS.[3] Where $\delta^{18}O$ records were ambiguous, they additionally used the non-sea salt sulfur/sodium (nssS/Na) summer peak (indicative of summer solstice) as well as H_2O_2 to ascertain the annual $\delta^{18}O$ maxima. They counted annual peaks in the remaining major ionic species to validate and confirm the accuracy of the age assignment. Validation of the oxygen isotope based dating was done using (in this order): nssS, Na^+, H_2O_2, Mg^{2+}, Cl^-, and Ca^{2+}. Further

confirmation of dating assignment was conducted using the Pb-enrichment time series wherein the 1979 spike in Pb enrichment was used as a tie-point. Total dating error is ±1 year.

Extensive care was taken in handling the ice core to avoid any introduction of contamination that could compromise the trace analysis. During collection process, handling, and sample preparation, no products containing fluoropolymer coatings came into contact with the ice cores. The samples were separated into 1 m ice core sections for packaging in polyethylene wrap and shipped frozen to the Canadian Center for Inland Waters (CCIW) in Burlington, Ontario, Canada. They were kept frozen at −35°C for four months prior to sectioning.

2.3 Sample Sectioning

I, along with assistance from Cora Young, John MacInnis and Cyril Cook, travelled to the CCIW, where we sectioned the ice cores in a −10°C freezer into discrete samples corresponding to individual years. Sectioning was done using stainless steel tools, cleaned with methanol (MeOH) (Omnisolv, 99.9%, EMD, ThermoFisher) before and after each sample. Ice core sections were placed into pre-cleaned 4 L high-density polypropylene bottles and kept frozen at −35°C prior to extraction and analysis.

2.4 Sample Extraction

I, along with assistance from John MacInnis, carried out extraction of the ice core samples, following training by Christine Spencer. Samples were thawed immediately

prior to extraction and 500 mL of the melted water was aliquoted into methanol-rinsed VWR-Polypropylene Wide Mouth bottles for extraction. Sub-samples for extraction were spiked with 30 µL of a surrogate mixture (Table 2.1), which acted as the internal standard (IS) to monitor recovery. Isotopically labeled IS's account for losses due to extraction procedure and compensate for matrix effects. Samples were shaken, sonicated for 10 minutes, and held for 30 minutes at room temperature.

Table 2.1. Analyte quantifier and qualifier ion transitions (m/z) and internal standards used for PFAA analysis. Internal standards (IS) were used to evaluate recovery and matrix effects, while instrument performance (IP) standards were used to evaluate matrix effects only. Precursor ion/product ion transitions (m/z) are indicated in brackets.

Analyte	Quantifier/Qualifier Ion Transition (m/z)	Internal Standard	Instrument Performance Standard
TFA	113 > 69		
PFPrA	163 > 119		
PFBA	213 > 169	$^{13}C_4$ PFBA (217/172)	$^{13}C_3$ PFBA (216/172)
PFPeA	263 > 219	$^{13}C_5$ PFPeA (268/223)	$^{13}C_3$ PFPeA (266/222)
PFHxA	313 > 269 / 313 > 119	$^{13}C_2$ PFHxA (315/270)	$^{13}C_5$ PFHxA (318/273)
PFHpA	363 > 319 / 363 > 119, 169	$^{13}C_4$ PFHpA (367/322)	
PFOA	413 > 369 / 413 > 169	$^{13}C_4$ PFOA (417/372)	$^{13}C_2$ PFOA (415/370)
PFNA	463 > 419 / 463 > 219	$^{13}C_5$ PFNA (468/423)	$^{13}C_9$ PFNA (472/427)
PFDA	513 > 469 / 513 > 219	$^{13}C_2$ PFDA (515/470)	$^{13}C_6$ PFDA (519/474)
PFUnDA	563 > 519 / 563 > 319, 269	$^{13}C_2$ PFUnDA (565/520)	$^{13}C_7$ PFUnDA (570/525)
PFDoDA	613 > 569 / 613 > 169	$^{13}C_2$ PFDoDA (615/570)	
PFTrDA	663 > 619 / 663 > 169	$^{13}C_2$ PFDoDA (615/570)	
PFTeDA	713 > 669 / 713 > 169	$^{13}C_2$ PFTeDA (715/670)	
PFHxDA	813 > 769 / 813 > 169	$^{13}C_2$ PFHxDA (815/770)	
PFOcDA	913 > 869 / 913 > 169	$^{13}C_2$ PFHxDA (815/770)	
PFBS	299 > 80 / 299 > 99	$^{13}C_3$ PFBS (302/99)	
PFHxS	399 > 80 / 399 > 99	$^{18}O_2$ PFHxS (403/103)	$^{13}C_3$ PFHxS (402/99)
PFHpS	449 > 80 / 449 > 99	$^{18}O_2$ PFHxS (403/103)	
PFOS	499 > 80 / 499 > 99	$^{13}C_4$ PFOS (503/99)	$^{13}C_8$ PFOS (507/99)
PFDS	599 > 80 / 599 > 99	$^{13}C_4$ PFOS (503/99)	
FOSA	498 > 78	$^{13}C_8$ FOSA (506/78)	
PFECHS	461 > 381 / 461 > 99	$^{18}O_2$ PFHxS (403/103)	

Targeted analytes included: trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFOcDA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptane sulfonic acid (PFHpS), perfluorooctane sulfonic acid (PFOS), perfluorodecane sulfonic acid (PFDS), perfluoroethylcyclohexanesulfonate (PFECHS), and perfluorooctanesulfonamide (FOSA).

Samples were concentrated using an OASIS® weak anion exchange (WAX) solid phase extraction (SPE) cartridge (6 cm^3, 150 mg, 30 μm). Cartridges were conditioned prior to sample loading with 5 mL 0.1% NH_4OH/MeOH, followed by 5 mL MeOH and 5 mL SPE-cleaned HPLC Grade water (Fisher). Following sample concentration, the cartridges were rinsed with 25 mM ammonium acetate buffer acidified to pH 4 with acetic acid, and centrifuged at 4000 rpm for 2 minutes to remove any residual water. Samples were eluted into two fractions: the first fraction was eluted with 6 mL of MeOH for FOSA, and the second fraction was eluted with 8 mL of 0.1% NH_4OH/MeOH for PFAAs. Both fractions were evaporated to dryness under a gentle stream of nitrogen and reconstituted in 0.5 mL 50/50 methanol-water containing the surrogate mixture (Table 2.1) to monitor matrix effects. Isotopically labeled IP's account for matrix effects and

instrumental drift and are typically used as a check. Reconstituted samples were sonicated for 5 minutes, vortexed and transferred to polypropylene vials for analysis.

2.5 Analysis

Ice core samples were analyzed by both liquid chromatography and ion chromatography. Liquid chromatography with mass spectrometry was performed to separate, analyze and quantify the different PFAA analytes. Major ion chromatography was performed to separate, analyze and quantify the different cations and anions in the samples.

2.5.1 Liquid Chromatography

I, along with John MacInnis prepared samples for analysis, while Christine Spencer operated the instrument, with already established analytical methods. I carried out the data interpretation, with training and assistance from Christine Spencer. Samples were analyzed using ultra performance liquid chromatography (Waters Acquity UPLC I) with tandem mass spectrometry (Waters Xevo® TQ-S, UPLC-MS/MS) detection operated in electrospray negative ionization mode. The mass analyzer was a tandem quadrupole mass spectrometer, operated in multiple reaction monitoring (MRM) mode. Common fragments that occur using this mode are $C_nF_{2n}^-$ for PFCAs and FSO_3^- (m/z 99) or SO_3^- (m/z 80) for PFSAs. For the long-chain PFAA (PFCAs > C4, PFSAs > C4, FOSA) analysis, samples were separated using a C18 column (Waters Acquity UPLC® BEH, 2.1×50 mm, 1.7 μm) with a water-methanol 2 mM ammonium acetate gradient method (Table 2.2). For the short-chain PFAA (PFCAs < C8, PFOS) analysis, samples

were separated using a Shodex RSPak column (2.0×150 mm, 5 µm) with a water-methanol 50 mM ammonium acetate method. Mobile Phase A was SPE-cleaned water and 50 mM ammonium acetate, adjusted to pH 9, and Mobile Phase B was MeOH. The isocratic LC method was 15 minutes, with a flow rate of 0.300 mL min^{-1}, at 20% H_2O and 80% MeOH. A summary of the inlet and mass spectrometric conditions are provided in Table 2.3. The conditions were the same for both methods except for column temperature which was 50°C for the long-chain PFAA analysis and 40°C for the short-chain PFAA analysis.

Table 2.2. Summary of chromatographic conditions for the long-chain PFAA analysis.

Time (minutes)	Flow rate (mL min^{-1})	% H_2O	% MeOH
0	0.400	75	25
0.5	0.400	75	25
5.0	0.400	15	85
5.1	0.400	0	100
5.6	0.400	0	100
7.0	0.550	0	100
9.0	0.400	75	25
12.0	0.400	75	25

Table 2.3. Summary of inlet and mass spectrometric conditions for both the long-chain and short-chain PFAA analyses.

Capillary Voltage (kV)	1.7
Cone Voltage (V)	10
Source Offset (V)	50
Source Temperature (°C)	150
Desolvation Gas Temperature (°C)	450
Cone Gas Flow (L hr^{-1})	150
Desolvation Gas Flow (L hr^{-1})	650
Collision Gas Flow (mL min^{-1})	0.15
Nebulizer Pressure (bar)	7.0
Column Temperature (°C)	50 / 40
Injection Volume (µL)	9.0

Analytes were quantified based on relative response to isotopically labeled instrument performance (IP) standards (Wellington Laboratories, Guelph, ON). Further details on recovery, standards, blanks and other calculations are covered in Section 2.6.

2.5.2 Major Ion Chromatography

Sub samples of the sectioned ice core (15 mL) were analyzed for major anions and cations. I carried out the major ion analysis for the anions, with training and assistance from Trevor Vandenboer and Jamie Warren. The Newfoundland and Labrador Department of Natural Resources did the cation analysis, as I did not have access to the instrument for this analysis on campus. Anions were measured by ion chromatography with conductivity detection and cations were quantified using inductively coupled plasma and optical emission detection. A range of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}) and other metals (e.g. iron and silicon), and anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) and organic acids (e.g. acetate, propionate, formate and butyrate) were measured.

I conducted anion analysis using a Dionex ICS 2100 Ion Chromatography System coupled to a conductivity detector, DS6 heated conductivity cell (Thermo Scientific, Mississauga, ON, Canada). Injection volumes were 1 mL using an autosampler (Dionex AS-DV) and preconcentrated on a concentrator column (TAC-ULP1, 5 mm x 23 mm). Anions were separated on an anion exchange column (Dionex™ IonPac™ AS19, 4 mm × 250 mm) with guard column (AG19, 4 mm × 50 mm) using gradient elution with potassium hydroxide at 1.5 mL min^{-1} flow rate. The eluent was suppressed (AERS 500 ion suppressor, 4 mm) before the analytes were measured. I prepared calibration

standards by serial dilution from the stock standard (Dionex Seven Anion Standard II), which were run with the sample analysis, check standards and analytical blanks. I calculated the LOD and LOQ values for the anions based on S/N 3 and 10, respectively (Section 2.7). Detection limits ranged from 0.07 – 927 ppb.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis for cations was performed by the Newfoundland and Labrador Department of Natural Resources, using an iCap 6500 Series ICP-OES (Thermo Scientific, Mississauga, ON, Canada). I prepared thirty ice core samples by acidifying 10 mL water samples with 2% (v/v) HNO_3 prior to analysis, and prepared calibration standards by serial dilution from the stock standard (Dionex Six Cation Standard). In addition to calibration standards, two check standards and a reagent blank were run every 20 samples. Yttrium was added inline as an internal standard. They analyzed each sample four times using the following settings: nebulizer pump flush rate 100 rpm, analysis pump rate 50 rpm, pump relaxation time: 20 s, RF power: 1150 W, nebulizer gas: 0.55 L min^{-1}, auxillary gas: 0.5 L min^{-1}. They quantified the detection limits based on instrumental detection limits, which ranged from 0.40 – 20 ppb.

2.6 Quality Assurance and Quality Control

Cartridge blanks were used to validate the integrity of the extraction method, and isotopically labeled standards were used to validate recovery and matrix effects. I calculated the internal standard recoveries, which are summarized in Tables 2.4 – 2.5.

Table 2.4. Recovery of IS in sample extracts. IS analytes with numbers refers to the different ion transitions (m/z). Samples (500 mL) were spiked with internal standard (30µL) prior to extraction. Recovery is based on peak area comparison to solvent standard. Mean (standard error) recovery reported for n=42 samples from the Devon Ice Cap.

IS	Recovery (%)
$^{13}C_4$ PFBA	89 (1)
$^{13}C_5$ PFPeA	79 (1)
$^{13}C_2$ PFHxA	90 (1)
$^{13}C_4$ PFHpA	94 (1)
$^{13}C_4$ PFOA	96 (1)
$^{13}C_5$ PFNA	102 (1)
$^{13}C_2$ PFDA	104 (1)
$^{13}C_7$ PFUnDA	99 (1)
$^{13}C_2$ PFDoDA	70 (1)
$^{13}C_2$ PFTeDA	31 (1)
$^{13}C_2$ PFHxDA	61 (2)
$^{13}C_4$ PFOS 80	101 (1)
$^{13}C_4$ PFOS 99	101 (1)
$^{18}O_2$ PFHxS 103	101 (1)
$^{18}O_2$ PFHxS 84	100 (1)
$^{13}C_3$ PFBS 80	101 (1)
$^{13}C_3$ PFBS 99	102 (1)

Table 2.5. Recovery of IP in sample extracts. IP analytes with numbers refers to the different ion transitions (m/z). Samples (500 mL) were spiked with instrument performance standard (30µL) prior to extraction. Mean (standard error) recovery reported for n=42 samples from the Devon Ice Cap.

IP	Recovery (%)
$^{13}C_3$ PFBA	110 (1)
$^{13}C_3$ PFPeA	96 (2)
$^{13}C_5$ PFHxA	105 (1)
$^{13}C_2$ PFOA	104 (1)
$^{13}C_9$ PFNA	108 (1)
$^{13}C_6$ PFDA	111 (1)
$^{13}C_2$ PFUnDA	109 (2)
$^{13}C_8$ PFOS 80	105 (1)
$^{13}C_8$ PFOS 99	104 (1)
$^{13}C_3$ PFHxS 99	104 (1)

Three samples were extracted in triplicate and one sample in duplicate to evaluate reproducibility. A composite mixture of Devon Ice Cap samples was prepared and for three types of QA/QC measures in triplicate: one sample was spiked with PFASs before extraction, one sample spiked with PFASs after extraction, and the third sample spiked with the internal standard and processed akin to the larger sample set. The pre-extraction and post-extraction spiked samples were compared to evaluate recovery and matrix effects. There were no quantifiable PFAA levels detected in the routinely analyzed methods blanks (SPE cartridge blanks, n=6). Method recoveries for the PFAAs ranged from 79 – 117% with the exception of PFOcDA ranging from 127 – 255%. PFOcDA recoveries indicated enhancement of analyte signal due to matrix effects and incorrect recovery and matrix correction due to using MPFHxDA as the internal standard. Since PFOcDA was below detection limit in all ice core samples, this was not further explored.

I evaluated matrix effects by comparing the peak area of IP compounds to peak areas at equivalent concentrations in a solvent standard. I evaluated recovery by comparing the recovered analyte concentration in the spike and recovery sample to the theoretical spiked concentration. Each sample was corrected for recovery and matrix effects by quantifying based on relative response to isotopically labeled standards added before extraction. A 15 level calibration curve was employed ranging from 0.02 – 8.5 ng mL^{-1}, along with analytical blanks. Analytical blanks (MeOH) and cartridge blanks were included in the method analysis. The method detection limit (MDL) was based on 3× the standard deviation of the cartridge blanks. The majority of the PFAA analytes were not

detected in the method blanks and were therefore below the instrument detection limit (IDL) (Table 2.6).

The limit of detection (LOD) and limit of quantitation (LOQ) were defined as concentrations corresponding to signal-to-noise (S/N) ratios of 3 and 10, respectively (Table 2.7). Detailed methods for LOD calculations are provided in Section 2.7.

Table 2.6. Method detection limit based on 3× the standard deviation of the blanks.

Perfluoroalkyl Substance	Method Blanks
TFA	<IDL*
PFPrA	<IDL
PFBA	<IDL
PFPeA	<IDL
PFHxA	<IDL
PFHpA	<IDL
PFOA	0.010
PFNA	0.0042
PFDA	<IDL
PFUnDA	0.0070
PFDoDA	<IDL
PFTrDA	<IDL
PFTeDA	<IDL
PFHxDA	<IDL
PFOcDA	<IDL
PFBS	<IDL
PFHxS	0.0036
PFHpS	<IDL
PFOS	0.0017
PFDS	<IDL
PFECHS	<IDL
FOSA	0.0055

*Analytes <IDL (instrument detection limit) were not detected in the method blanks.

Table 2.7. Instrument limit of detection (LOD) and quantitation (LOQ) for PFAAs.

Compound	Ion	LOD (pg L^{-1})[1]	LOQ (pg L^{-1})[2]	Reproducibility[3]
TFA		151	503	5.95
PFPrA		154	514	10.9
PFPrA		39.8	133	7.37
PFPeA		10.4	34.7	8.53
PFHxA	269	2.52	8.41	9.67
	119	14.6	48.5	11.9
PFHpA	319	3.05	10.2	11.0
	169	1.79	5.96	11.4
PFOA	369	2.44	8.12	9.76
	169	1.44	4.81	3.48
PFNA	419	3.49	11.6	6.48
	219	1.44	4.80	7.67
PFDA	469	3.75	12.5	2.50
	219	1.18	3.94	15.1
PFUnDA	519	4.72	15.7	1.10
	269	1.17	3.91	4.25
PFDoDA	569	3.61	12.0	9.53
	169	1.54	5.12	9.67
PFTrDA	619	3.21	10.7	11.6
	169	0.98	3.25	5.65
PFTeDA	669	3.73	12.4	5.79
	169	1.02	3.39	6.02
PFHxDA	769	4.64	15.5	4.42
	169	1.85	6.16	1.23
PFOcDA	869	24.4	81.2	9.90
	169	31.9	106	13.4
PFBS	80	0.91	3.04	12.9
	99	3.62	12.1	7.56
PFHxS	80	0.37	1.23	7.40
	99	1.83	6.09	6.76
PFHpS	80	1.16	3.86	6.30
	99	1.43	4.77	13.2
PFOS	99	1.27	4.23	25.8
PFDS	80	0.28	0.94	15.0
	99	1.33	4.44	9.21
PFECHS	99	0.94	3.14	3.25
	381	1.09	3.63	4.80
FOSA		0.18	0.59	14.8

[1]LOD is concentration corresponding to signal-to-noise (S/N) ratios of 3. [2]LOQ is concentration corresponding to S/N of 10. [3]Reproducibility is given by the percent relative standard deviation for triplicate extraction and analysis of a sample.

2.7 Data Handling

I used the instrument software package, MassLynx, to integrate chromatographic peaks for analytes using two precursor-to-product ion transitions including the data for the IS and IP in each analyte. Using this, MassLynx outputs the peak area, calculated concentration, % recovery of internal standard and signal-to-noise (S/N) ratio. I also did a check to see if similar results were obtained by doing calculations by hand. Concentrations were corrected for extraction efficiency and matrix effects since the calibration curve and quantification is based on relative response to the internal standards, providing a built-in correction factor. For analytes with two transitions, I calculated the average concentration if the difference between transitions was <15%. I then corrected the concentrations for the initial and final sample volumes used. The IS and IP percent recoveries can be compared and used to calculate the extraction efficiency and matrix effects of the samples.

Matrix effects (ME) are calculated as follows:

$$\mathrm{ME} = \left[\frac{\mathrm{IP}_{\text{Peak area sample}} - \mathrm{IP}_{\text{Peak area standard}}}{\mathrm{IP}_{\text{Peak area standard}}}\right] \times 100\%$$

Signal enhancement is occurring if ME > 100% and signal suppression is if ME < 100%. An ME closest to zero represents an ideal absence of matrix influence.

Extraction efficiency (EE) is calculated as follows, where SSB is spiked sample before and SSA is spiked sample after extraction:

$$\mathrm{EE} = \left[\frac{\mathrm{IS}_{\text{Peak area SSB}}}{\mathrm{IS}_{\text{Peak area SSA}}}\right] \times 100$$

Fluxes for each analyte were calculated and given in ng m^{-2} yr^{-1}. Fluxes were calculated as follows:

$$\text{Flux} = \left[\frac{\text{Analyte Concentration } (ng\ L^{-1}) \times \text{ Total ice volume per year (L)}}{\text{Area } (m^2)}\right]$$

$$(\text{Area} = \pi r^2 \text{ where } r = 4.5\text{cm})$$

The limit of detection (LOD) refers to the lowest quantity that can be reliably distinguished from the blank. The limit of quantitation (LOQ) refers to the lowest quantity that can be quantified accurately. I calculated these values as follows:

1. From the MassLynx data, MeOH blank runs and standard calibration curves were used to calculate LOD. Five standard calibration curve sets were run over 2 days.
2. The chromatographic data for each blank and standard from MassLynx was transferred to Excel, which provided the retention time and signal height in counts for each chromatogram.
3. For the MeOH blanks, two blanks each were chosen: a blank that was run before and one run after the calibration curve. For each of the two blanks, the standard deviation (SD) of the counts and the average (avg.) of those two standard deviations were calculated.
4. For each standard in the curve, the avg. noise was calculated by taking the avg. of the counts directly before the peak in the chromatogram. The max value in the

peak was also determined and then the signal was calculated by subtracting the avg. noise from the max value. (Signal = Max Value − Avg. Noise)

5. The signal was divided by the avg. SD of the blanks to obtain the Signal/Noise ratio (S/N = signal/avg. SD). The S/N was determined for each of the standards and then S/N vs. calculated concentration (ng mL^{-1}) of the standards was plotted.
6. The linear regression of the plot was determined by letting y-intercept = 0.
7. LOD = 3/m and LOQ = 10/m (m = slope) (y = mx).
8. Steps 2-7 were repeated for two more sets of calibration curves with two blanks. Overall LOD and LOQ values were obtained by averaging the avg. of the 3 LOD and 3 LOQ values, respectively.
9. Steps 1-8 were repeated for each analyte and each ion transition.
10. The LOD and LOQ values were compared to the uncorrected concentrations (ng mL^{-1}) of the analytes determined by mass lynx. Corrected concentration values that were <LOD/LOQ were replaced with ½ LOD/LOQ.
11. Statistics on these values were obtained using the SD of the 3 slopes and the avg. of the 3 slopes. The SD was divided by the avg. and multiplied by 100 to get % precision. The SD of the 3 LOD values was divided by one LOD value and multiplied by 100 to get the relative SD (relative SD=(SD of 3 LOD values/1 LOD value)*100). The % Precision and relative SD were below 15% for all analytes suggesting the LOD/LOQ values are reasonable.
12. The method detection limit (MDL) values were calculated by multiplying the LOQ values by 0.5 mL (extract volume) and dividing by 500 mL (theoretical

sample volume) in order to report MDL and LOQ that were in units (ng L^{-1}) directly translatable to sample concentrations.

2.8 Air Mass Transport Modelling

To trace the origins of air masses arriving at the sampling site on Devon Ice Cap and characterize source regions, I computed 5-day air mass back trajectories using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model.[4] I performed the trajectory analysis using the global NCEP-NCAR Reanalysis meteorology data set at 2.5 degrees resolution. I initiated back trajectories at 2175 meters AMSL at the Devon Ice Cap sample site location, every 6 hours for a month-long duration and each trajectory was run backwards for 120 hours. I compiled monthly back trajectories to create yearly trajectories for 1994 and 2013. I then computed quantitative geographic sector assignment in Igor Pro by running a custom-built procedure on raw trajectory end point latitude and longitude coordinates.[5] Back trajectory end points were thus assigned to one of four quadrants (northeast, northwest, southeast, southwest) centered on the sampling site location. Raw end point output files for entire years were integrated and sorted before being imported to Igor Pro for sector assignment. The integrity of the data was qualitatively verified as unchanged and intact after the integration and sorting procedure was performed by visually inspecting the re-plotted trajectories using supplemental software designed for importing raw HYPLIT data into Igor Pro.[6]

Following the air mass back trajectory analysis; Alison Criscitiello used this data to compute air parcel back trajectories, which further allow us to examine air mass

moisture source regions. For this analysis, she initiated daily, 10-day back trajectories at the same location, for years 1994 and 2013. Residence time analysis was then used to identify air mass transport densities for those two years.[7] This approach analyzes a large number of trajectories to reduce uncertainties, develop reliable pathways of airflow and account for variations in transport speed and direction.[8] For this analysis, Alison Criscitiello summed the total number of trajectory endpoints within each equal-area pixel, and then divided by the zonal distance between the Devon ice core sampling site and each pixel to remove concentric patterning. The air mass transport densities were scaled on a 0-1 scale, for the low-elevation air masses (0–500 m above terrain), which are more likely to be representative of evaporation moisture source.

2.9 Conclusions

This chapter described the detailed method used for the ultra-trace detection of PFASs in ice core samples. During all steps of sample collection, preparation, extraction, and analysis, many precautions were undertaken to avoid contamination and sample loss. We used methods previously outlined for this type of analysis and I did extensive QA/QC to monitor the recovery of our sample extracts. With increased sampling and analytical capabilities, I am confident in the methods we applied for the analysis of PFASs in ice core samples.

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3 Continuous Non-Marine Inputs of Per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record

3.1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of compounds that have been used in surfactants and polymers for over 60 years.[1] Perfluoroalkyl acids (PFAAs) are persistent contaminants that are ubiquitous in the environment. Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are two of the most widely known and studied groups of PFAAs.[1,2] PFAAs are prevalent in remote locations, such as the Arctic,[3] due to their ability to undergo long-range transport through the atmosphere and/or the ocean.[4] Long-range transport can be a combination of both direct transport and indirect formation. With direct transport, PFAAs are directly transported in their carboxylic (PFCA) or sulfonic (PFSA) acid form to remote locations. This can occur via oceanic water currents or by marine aerosol formation.[5] With indirect formation, PFAAs are produced through chemical transformation of PFAS precursors in the atmosphere.[6] These compounds are environmentally persistent and longer chain acids (>6 carbons) have a tendency to bioaccumulate and biomagnify in food webs.[3,7,8]

In the atmosphere, volatile and semi-volatile precursors such as fluorotelomer alcohols (FTOHs), N-alkyl perfluoroalkane sulfonamides/sulfonamidoethanols (NAFSAs/NAFSEs) and heat transfer fluids (i.e. chlorofluorocarbon-replacements) undergo oxidation in the gas phase to form PFAAs.[6,9,10] The atmospheric lifetime and persistence of these precursors is long enough to reach remote locations by wind and air

transport, before subsequently oxidizing to the corresponding PFAAs and depositing to remote locations.[11,12]

Once these PFAAs are formed indirectly in the atmosphere, they will undergo wet or dry deposition. Further transport can occur via ocean currents[13–15] and marine aerosols.[16] PFAAs are highly acidic, surface-active compounds, usually present as anions in the aqueous phase under environmental conditions.[17] These surface-active compounds will concentrate at the air-water interface and are therefore expected to be in the sea surface microlayer (SSML) and to be present in marine aerosols.[18]

The long-range transport mechanisms of these compounds can be elucidated through the collection and analysis of remote samples, such as ice core samples. Ice caps receive their contamination solely from atmospheric deposition due to their high elevation, and preserve a temporal record of that deposition. Devon Ice Cap, located on the Devon Island in Nunavut, Canada, was previously sampled for PFAAs in May of both 2006 and 2008 through collection from the sidewall of a snow pit.[12,19] This ice cap has a high latitude and elevation[20] and is not expected to receive any local or oceanic sources of contamination. These previous studies detected PFAAs in snow profiles that spanned a 10 – 14 year period in deposition. In this study, a 15 m ice core was collected in 2015, allowing me to examine PFAA deposition over a much longer (38 year) period. Within this chapter I discuss: (1) PFAA deposition and temporal trends; (2) homologue patterns and volatile precursor mechanisms; (3) transport of PFAAs to the Arctic via ion tracer analysis; and (4) PFAA source regions via transport modelling. This work represents the first multi-decadal analysis of PFAAs in an ice core from the summit region (2175 m above mean sea level) of a large Arctic ice cap.

3.2 Methods

Methods are similar to those outlined in reference [19]. Further details on sample collection, preparation, extraction, analysis, and transport modelling are provided in Chapter 2 – Methodology.

3.3 Results and Discussion

3.3.1 PFAA Concentrations and Fluxes in the Devon Ice Cap: Comparisons to Previous Studies

A comprehensive analysis of perfluoroalkyl acid (PFAA) and FOSA annual deposition on the Devon Ice Cap was carried out on ice core samples dating from 1977 – 2015. In general, PFCAs from TFA (C2) to PFTrDA (C13) were detected on the Devon Ice Cap with concentrations ranging from <3.21 pg L^{-1} to 208 ng L^{-1} (Table A.1). Concentrations of all of the PFAS analytes detected in a single year are represented in Figure 3.1. PFCAs from TFA to PFUnDA (C2 – C11) were detected in almost every sample, with the exception of PFBA and PFUnDA, which were not detected in one year each and PFPeA, which was not detected in 5 separate years. The long-chain PFCAs including PFDoDA and PFTrDA were only quantifiable in <3 years, while PFTeDA, PFHxDA, and PFOcDA were <LOQ throughout the 38 year time period and will not be discussed further. TFA had the highest concentrations of all the PFCAs (6.56 – 208 ng L^{-1}), with PFPrA having the second highest concentrations. PFSAs including PFBS, PFHpS and PFOS, as well as FOSA were detected on the Devon Ice Cap with concentrations ranging from <0.18 pg L^{-1} to 391 pg L^{-1} (Table A.2). PFOS was detected in every sample while PFBS and PFHpS were only detected >LOD in two years.

Evidence of the presence of PFHxS, PFDS and PFECHS was sought, but not found. FOSA was detected >LOD in most samples up until 2000 and only in three samples after 2000.

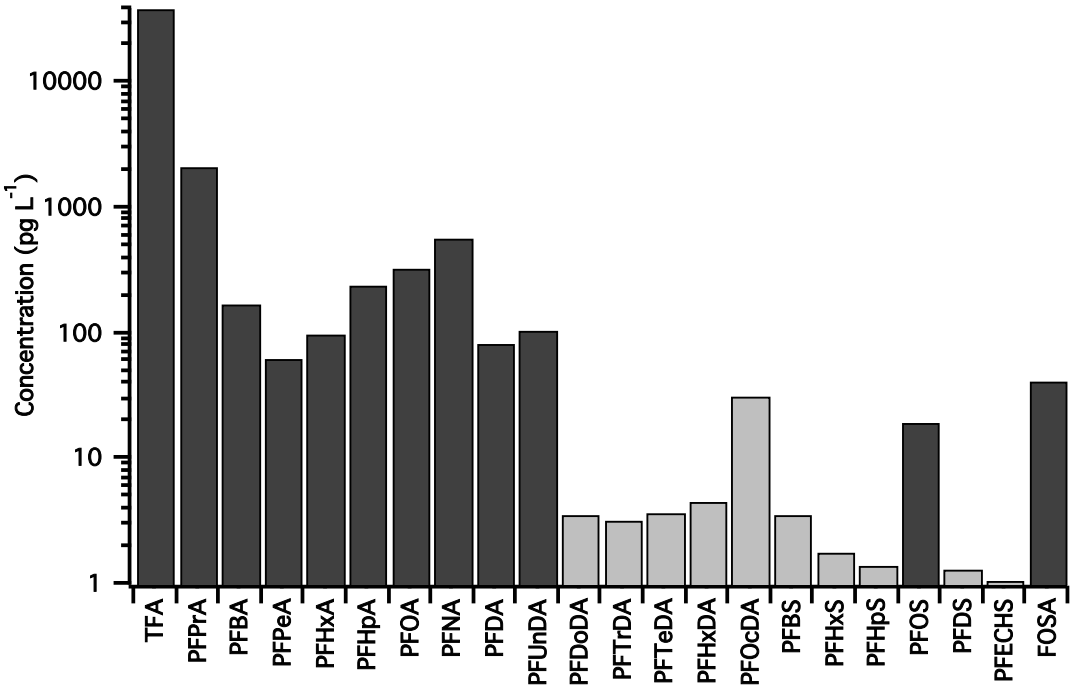

Figure 3.1. Concentrations of all the detected PFAS analytes for the year 1996, as a single representative year. Measurements in light grey are <LOD.

Concentrations (pg L^{-1}) of the PFAAs were converted to fluxes (ng m^{-2} yr^{-1}) (Tables A.3-A.4) to determine annual deposition of these compounds in the Canadian Arctic. Annual snow accumulation was 0.15 – 0.64 m yr^{-1}, which is consistent with 0.22 – 0.24 m wet equivalents yr^{-1} reported by Pinglot et al.,[21] for Devon Ice Cap from 1963-2000. Fluxes of PFAAs, including PFOA to PFUnDA (C8 – C11) and PFOS, were compared to fluxes of these PFAAs in two previous samples collected from snow pits on Devon Ice Cap in 2006[12] and 2008.[19] The data sets generally agree within the uncertainty of the measurements, with the exception of PFOS (Figure 3.2).

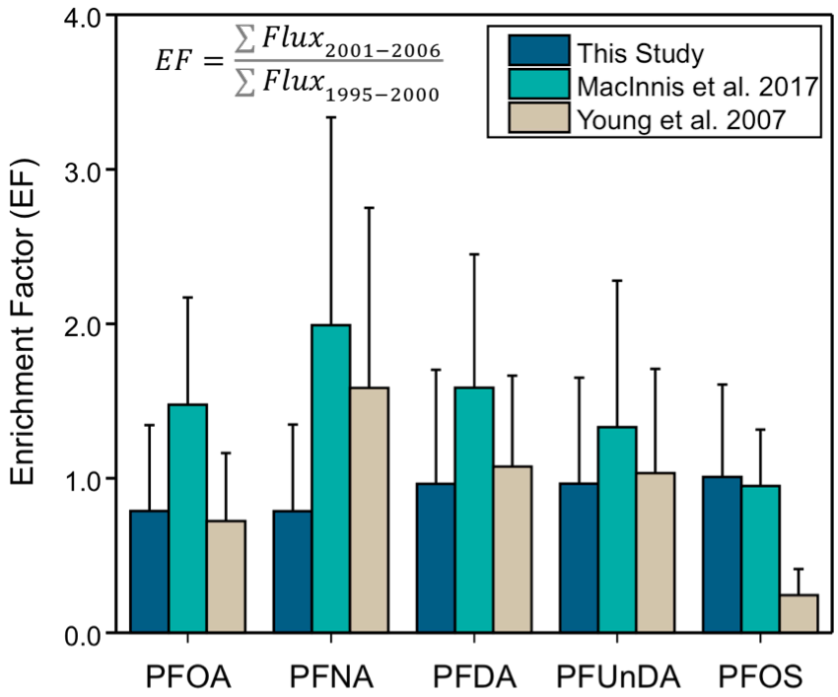

Figure 3.2. Calculated enrichment factor comparison between the sums of PFAA fluxes for 2001 – 2006 and 1995 – 2000, for the three Devon Ice Cap studies. The data sets generally agree albeit some subtle differences (i.e. the mean +/- uncertainty overlap between the three studies), the exception being PFOS.

These slight discrepancies between Devon Ice Cap studies could be the result of multiple factors. In the 2006 study, there was limited availability of isotopically labeled and native standards of sufficient purity. The current study represents an improvement in analytical methods since that time, both in terms of instrument detection limits and accuracy. The 2006 and 2008 sampling strategies are also in contrast to the current approach of ice core drilling. In the earlier efforts, depth samples were obtained by horizontal cylindrical sampling the face of an ice pit (2006) and vertically sampling the face of a snow pit continuously (2008). Those datasets likely represent semi-continuous depth measurements. In the current method, ice cores were obtained using a custom drill designed for Arctic sampling and conventional practices in ice sampling for temporal profiling.[20,22] Lastly, the Devon Ice Cap sampling locations in the earlier research were

not at the summit of the ice cap as in the current research. These differences in location may have resulted in some variability in fluxes. The most accurate temporal record of atmospheric deposition is obtained at the summit of an ice cap; thus, the current research is hypothesized to be a better representation of PFAA deposition to Devon Island.

Concentrations of PFCAs and PFSAs detected in this study are comparable to a number of other studies as summarized in Chapter 1. Comparable levels of PFCAs ranging from PFPeA to PFUnDA were detected in remote snow core and surface snow samples from Cole Gnifetti,[23] Longyearbreen,[24] and from glaciers on the Tibetan Plateau and Lake Namco.[25] Short-chain PFCAs had higher concentrations than other PFCAs detected in precipitation, lake and river water samples.[26–29] In general, concentrations of the PFCAs were much lower in the Arctic and Atlantic Oceans compared to the Devon Ice Cap concentrations. PFOS and FOSA concentrations were variable among all studies with no discernable trend for sample matrix or sample site.

3.3.2 Air Mass Transport Density Analysis

The use of air mass transport models is a commonly employed interpretation technique in understanding atmospheric observations. Previous studies using back trajectory analysis of air masses[30,31] have provided evidence for atmospheric LRT to the Devon Ice Cap from North America and Eurasia. Air masses on Devon Island originated three times more often from populated regions of Northern Europe and Asia compared to North America, and that Southern and Eastern Asia were significant source regions. Little variation was observed in Devon Ice Cap air mass source regions over the time period 1994 – 2008.[30] Previous studies on spatial patterns of pollen deposition in the High Arctic

further support these findings. Devon Ice Cap is located within an air mass boundary between 74° N and 76° N, between sites north of 76° that receive dominantly Eurasian pollen sources and sites south of 74° that receive dominantly North American pollen sources.[32] Devon Ice Cap therefore receives air masses and pollen/pollutant sources from both North America and Eurasia.

To do the HYSPLIT modelling, I chose the reanalysis meteorological data set, as it is the only data set that encompasses global data that dates back to 1977. A test was performed to determine whether trajectory arrival height influences the trajectory modelling and geographical sector assignment, by varying the back-trajectory arrival heights,[33] and found no influence on the quantitative back trajectory analysis with arrival height. Trajectories were initiated every 6 hours to increase the number of data points and reduce bias. This parameter was selected based on previous studies where back-trajectories were initiated every 6 hours for the long-term study of pollutant transport.[30,34] Finally, each trajectory was initiated every 3 hours and run 5 days backwards to determine the potential influence of LRT on our observations. This parameter was set since the HYSPLIT program limits frequency back trajectories to a maximum of 5 days and running a trajectory 7 – 10 days backwards leads to higher uncertainty in air mass origin.[35]

Figure 3.3 illustrates the air mass back trajectory models for 1994 and 2013. I modeled the year 1994 to compare to the Meyer et al. study and found similar results using these methods. Eurasian regions were among the dominant air mass source areas. Because of the unusual PFAA observations in 2013, I also examined this year to see if there were any transport anomalies, but found both years (1994 and 2013) to be

comparable with one another. A geographical sector analysis was applied to quantitatively assign the source region sectors where these air masses are originating. I calculated the percentage of air masses arriving from each sector (NE, NW, SE, SW) and found them to be equivalent, with an average of 25 ± 5.3 % for 1994 and 25 ± 2.2 % for 2013, for each sector. This analysis confirms that Devon Ice Cap is impacted by air masses from both North America and Eurasia.

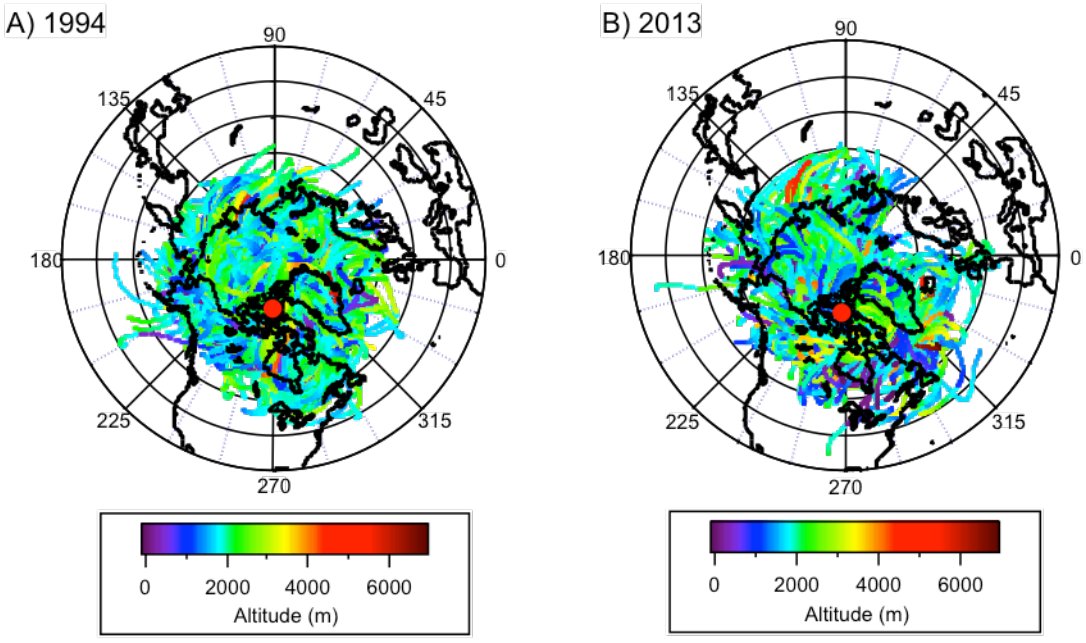

Figure 3.3. 5-Day back trajectory HYSPLIT model for Devon Ice Cap, for the years a) 1994 and b) 2013. Devon Ice Cap location is indicated by the red dot.

Air mass transport densities have previously been employed for investigating probable source regions and flow pathways of air masses in the Canadian Arctic.[36] Figure 3.4 illustrates the air mass transport density analyses calculated using the HYSPLIT model for Devon Ice Cap for the years 1994 and 2013. The year 1994 was again selected to compare to previous trajectory analyses and 2013 was examined to identify any transport anomalies. Both years were again found to be comparable. Air mass transport

densities for both 1994 and 2013 reveal elevated residence time densities in parts of Asia, and particularly high residence time densities along the west coast of Greenland.

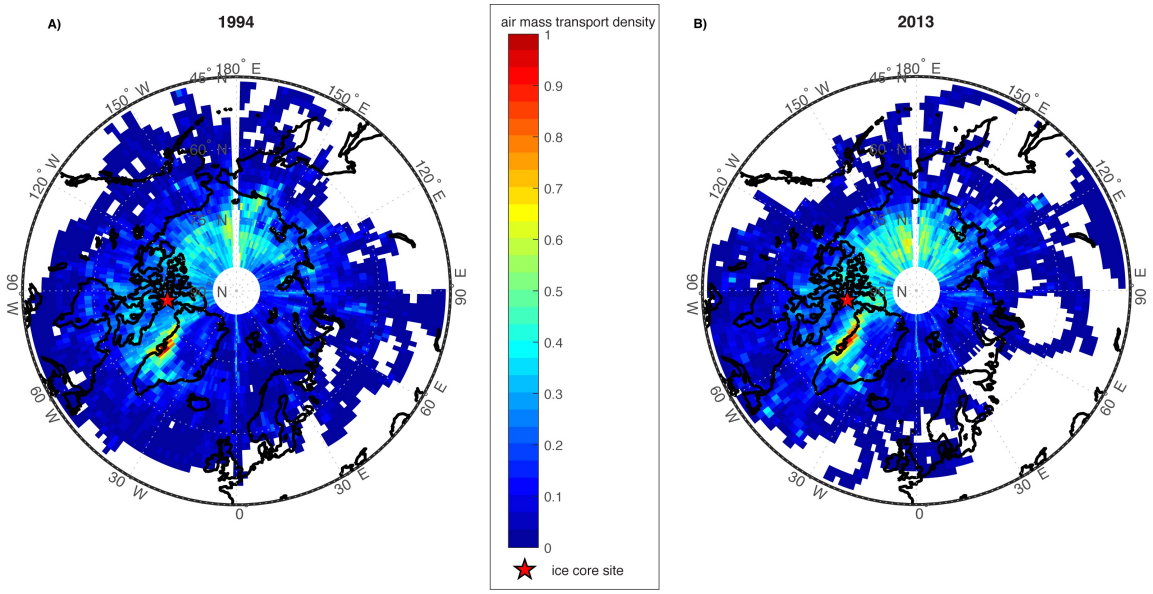

Figure 3.4. Air mass transport density maps (scaled 0-1) for air parcels reaching the Devon Ice Cap ice core site (red star) for the years a) 1994 and b) 2013.

3.3.3 PFCA Deposition and Temporal Trends on Devon Ice Cap

The temporal trends of short-chain PFCAs (C2 – C4) are discussed in more detail in Chapter 4. Annual fluxes of PFCAs ranged from <LOD to 4.44×10^4 ng m^{-2} yr^{-1}. In general, all PFCAs demonstrated an increase in flux after 1985 (Figures 3.5 – 3.6), but with diverging trends from 1995 – 2015.

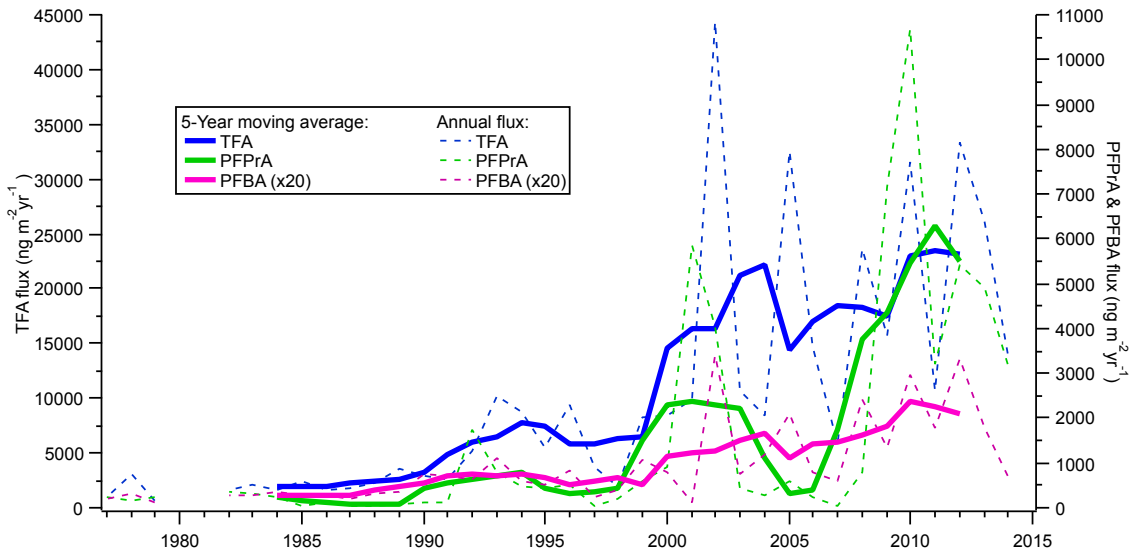

Figure 3.5. Temporal flux trends for the short-chain PFCAs including TFA, PFPrA and PFBA. Dotted lines represent annual fluxes and solid lines are the 5-year moving averages of the fluxes.

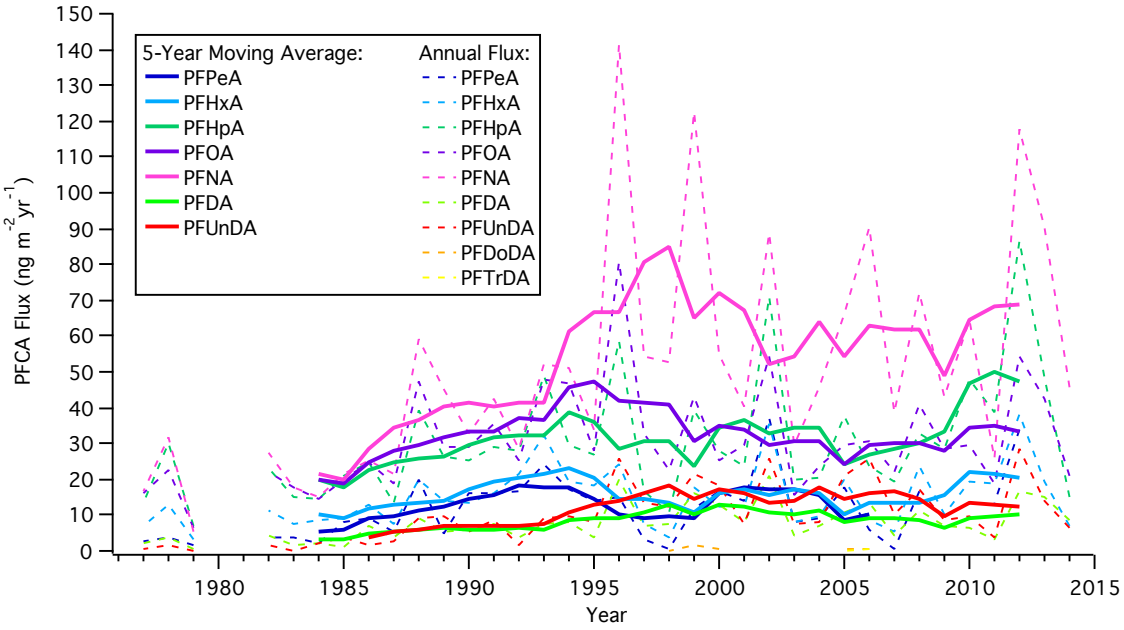

Figure 3.6. Temporal flux trends for the long-chain PFCAs including PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA. Dotted lines represent annual fluxes and solid lines are the 5-year moving averages of the fluxes.

Various glaciology studies have shown that Devon Ice Cap has experienced strong summer warming since 2000 and especially after 2005.[37–39] This is consistent with Inuit traditional knowledge of overall warming in the Arctic.[40] The variability in fluxes within the past 15 – 20 years could, therefore, be partially attributed to melting effects. When melting events occur, the ability to discern temporal trends in chemical deposition of various compounds can be compromised by the percolation of meltwater or elution of particles by meltwater flow.[41,42] These melting events could bias annual flux measurements of PFAAs in ice core samples during the melt period, since PFAAs on the ice cap surface can be eluted into the snowpack, before refreezing at ice layer interfaces where temperatures at depth are below the pressure melting point.[38] One study has examined elution behavior of PFAAs from a melting snowpack and found that the elution of PFAAs is largely driven by water solubility in the snowpack.[43] This melting has likely happened periodically over the last 15 – 20 years, thereby blurring to some extent, the vertical profile. However, I expect any melting that occurred to have primarily affected the seasonal trends. Variability of ± 1 year could be caused by inaccuracies in dating and/or error associated with ice core sectioning. To circumvent the compounding impacts of recent melt events and consequent meltwater percolation, and any error associated with ice core dating and sectioning, a 5-year moving average was applied to the flux measurements, thereby facilitating long-term temporal trend analysis of PFAS deposition to Devon Ice Cap.

Both PFOA and PFNA fluxes have increased from 1977 up until at least 1995 (Figure 3.7). In the period post-1995 until 2013, fluxes have plateaued, with <25 ng m^{-2} yr^{-1} variance in annual flux. From 2012 to 2015 a large decline in PFOA and PFNA

fluxes is apparent. The decrease in flux post-2012 was noted for the entire suite of PFCAs (Figures 3.5 – 3.6).

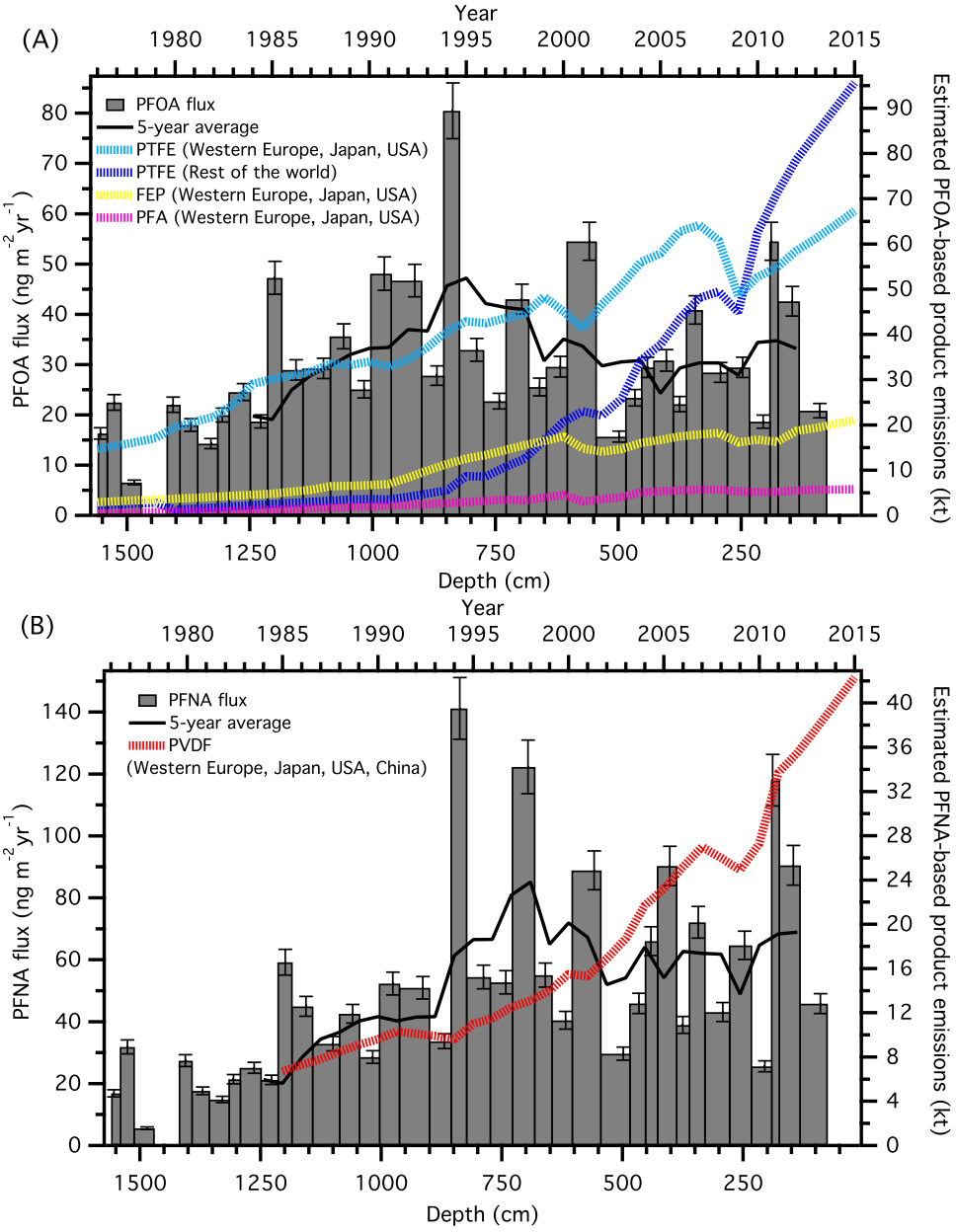

Figure 3.7. Annual deposition fluxes on Devon Ice Cap: a) PFOA and b) PFNA. The solid black line represents the 5-year moving average and the dotted coloured lines represent the estimated and reported consumption or production volumes of PFOA-based products including polytetrafluoroethylene (PTFE), perfluorinated ethylene-propylene copolymers (FEP), perfluoroalkoxyl polymers (PFA), and related ammonium and sodium salts (APFO/NaPFO), as well as PFNA-based products including polyvinylidene fluoride (PVDF) and related ammonium salts (APFN).[44]

This most recent decrease in PFCA fluxes could be due to melting events, or ice core dating and sectioning inaccuracies, but it also corresponds to anticipated PFCA emission reductions through the United States Environmental Protection Agency (EPA) PFOA Stewardship Program,[45] as well as the Canadian Environmental Performance Agreement.[46] In 2006, the EPA invited eight major fluoropolymer and fluorotelomer manufacturers to commit to eliminating emissions and product content levels of PFOA, precursor compounds, and related longer chain length homologue chemicals. Corporations voluntarily committed to achieving a 95% reduction by 2010, measured from a year 2000 baseline, and full elimination of these products and emissions by 2015.[45] In Canada, the federal government established The Environmental Performance Agreement with the same commitment between Environment and Climate Change Canada (ECCC), Health Canada and four major manufacturers with known organofluorine products in Canadian commerce.[46] As of 2016, all companies participating in the PFOA Stewardship Program and Environmental Performance Agreement reported they had met the goals of the Program (Tables A.5 – A.6). As part of both agreements, all major manufacturers reduced their production and emissions of PFOA and related compounds by at least 95% from 2006 – 2010. The observed decrease in PFOA and PFNA flux from 2012 – 2015 cannot solely be attributed to these phase-outs, since it would be expected that the phase out would cause a large decrease in PFCA deposition between 2006 and 2010 and a small decrease after 2012. It is probable that existing products continued to emit after the stewardship program took effect, which could delay the detection of this effect.[4] This is evident in temporal trend analysis in

Canada and the U.S. such as in human blood, freshwater fish, and non-migratory birds, which do not show any declines in PFCAs from 1990s to 2012.[47,48]

In addition, other historical and on-going sources of PFAS have emerged. Manufacturers that were not signatories to the PFOA stewardship program have been producing PFAS since 1985. China started polytetrafluoroethylene (PTFE) production around 1985 and was producing up to 60 kilotonnes (kt) in 2015.[44] Some manufacturers have emerged more recently that produce PFAAs and precursor compounds.[44,49] In general, from 2000 onward, long-chain PFCAs have been phased-out through regulation or voluntary reduction by major producers in Japan, Western Europe, the United States and Canada.[44,50] Meanwhile, new manufacturers (e.g. China) have begun producing these long-chain PFCAs and their precursors.[49] The total estimated annual emissions of PFBA to PFTeDA for Canada, the United States, Western Europe, and Japan were 25 – 50 t yr^{-1} in 2010, while estimated emissions of PFBA to PFTeDA were 40 – 193 t yr^{-1} in China in 2013.[44] Thus, global emissions of PFAAs and their precursors have not decreased significantly, which is consistent with observed temporal trends on Devon Ice Cap. Furthermore, the phase-out has created a market for numerous alternative fluorinated products,[51,52] some of which may be precursors to long-chain PFCAs. Observed temporal trends in PFAA fluxes may represent combined-effects of the stewardship program in North America and increasing production and emissions in other regions.

3.3.4 PFSA and FOSA Deposition and Temporal Trends on Devon Ice Cap

The observed concentrations of PFSAs and FOSA correspond to annual fluxes from <LOD to 80.3 ng m^{-2} yr^{-1} (Table A.4). Since PFBS and PFHpS were only detected

in three samples, there are no observable trends. PFOS and FOSA each show distinct temporal trends. PFOS occurred at consistent levels below 10 ng m^{-2} yr^{-1}, with an anomaly (80 ng m^{-2} yr^{-1}) detected in 2012 (Figure 3.8a). FOSA was measured in almost every year from 1977 – 2000 with fluxes increasing until 1995. After 2000, FOSA was only detected in three samples with levels <0.76 ng m^{-2} yr^{-1} (Figure 3.8b). FOSA is a known volatile precursor and can degrade to PFOS;[9] however, PFOS was continually measured after 2000, whereas FOSA was not. In addition, there was no correlation between PFOS and FOSA measurements (Table 3.1). This suggests FOSA is not the primary source of PFOS to the Devon Ice Cap.

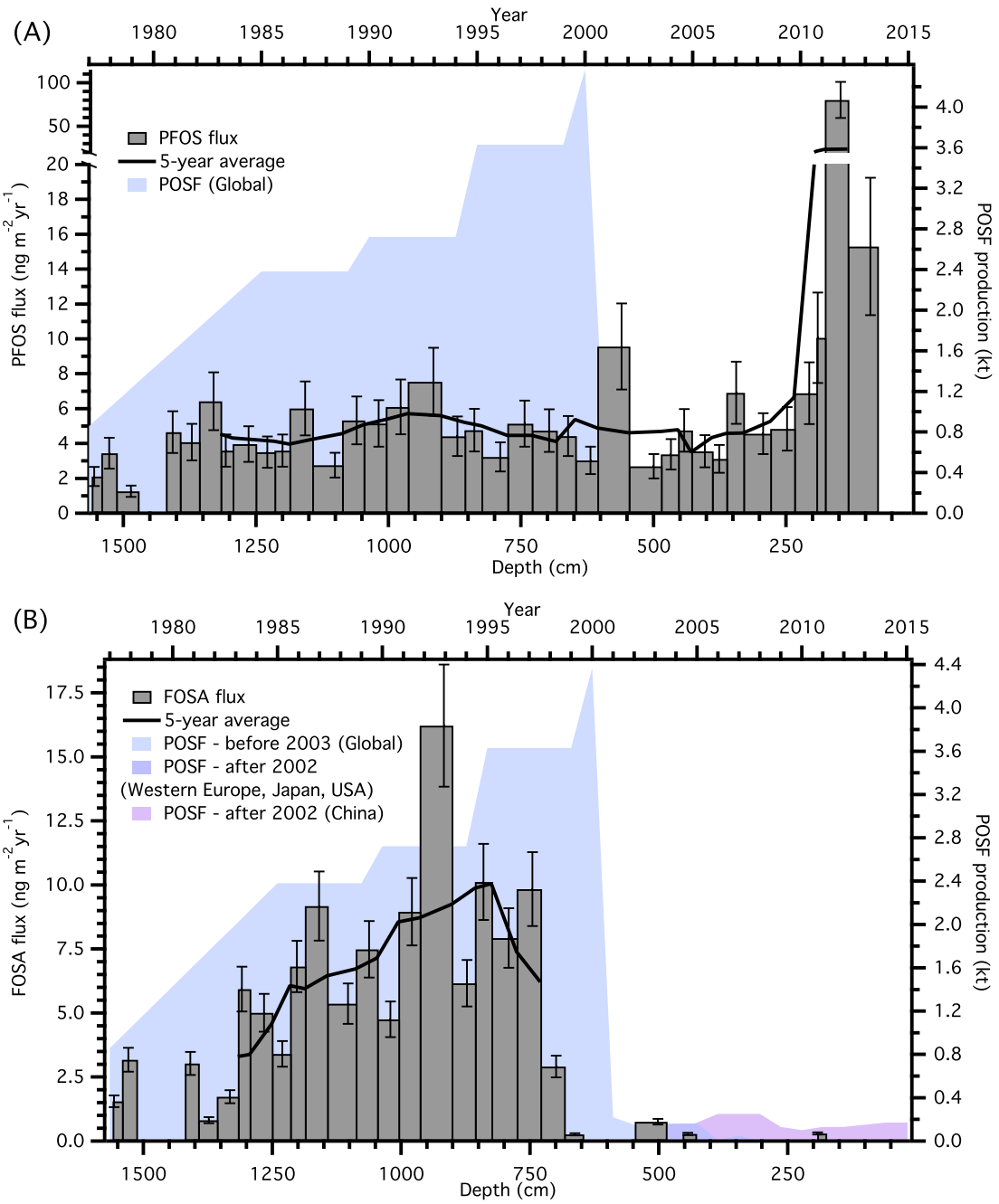

Figure 3.8. Annual deposition fluxes on the Devon Ice Cap: a) PFOS and b) FOSA with global POSF production (kt) from 1977 – 2003 and POSF production for Western Europe, Japan, USA and China from 2003 – 2015.[44,53] Solid black lines represent 5-year moving averages.

Table 3.1. Coefficients of determination (R^2) and statistical significance ($p<0.0001$) (bold) for PFAAs (n=30). Weak correlations (0.3 – 0.5) (green), moderate correlations (0.5 – 0.7) (blue) and strong correlations (0.7 – 0.99) (red). PFOS and FOSA did not correlate (R^2=0.037; p=0.2517)

	TFA	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFBS	PFHpS
PFPrA	**R^2= 0.455**													
	p<0.0001													
PFBA	**R^2= 0.772**	**R^2= 0.517**												
	p<0.0001	**p<0.0001**												
PFPeA	R^2= 0.160	R^2= 0.009	R^2= 0.308											
	p= 0.0142	p= 0.5737	p= 0.0004											
PFHxA	**R^2= 0.424**	R^2= 0.271	**R^2= 0.705**	**R^2= 0.668**										
	p<0.0001	p= 0.0010	**p<0.0001**	**p<0.0001**										
PFHpA	**R^2= 0.538**	**R^2= 0.379**	**R^2= 0.789**	**R^2= 0.505**	**R^2= 0.889**									
	p<0.0001	**p<0.0001**	**p<0.0001**	**p<0.0001**	**p<0.0001**									
PFOA	R^2= 0.285	R^2= 0.080	R^2= 0.332	R^2= 0.298	**R^2= 0.437**	**R^2= 0.527**								
	p= 0.0007	p= 0.0889	p= 0.0002	p= 0.0005	**p<0.0001**	**p<0.0001**								
PFNA	**R^2= 0.389**	R^2= 0.067	R^2= 0.284	R^2= 0.095	R^2= 0.186	R^2= 0.334	**R^2= 0.708**							
	p<0.0001	p= 0.1207	p= 0.0007	p= 0.0633	p= 0.0077	p= 0.0002	**p<0.0001**							
PFDA	**R^2= 0.368**	R^2= 0.032	R^2= 0.215	R^2= 0.129	R^2= 0.134	R^2= 0.246	**R^2= 0.592**	**R^2= 0.865**						
	p<0.0001	p= 0.2927	p= 0.0039	p= 0.0289	p= 0.0261	p= 0.0018	**p<0.0001**	**p<0.0001**						
PFUnDA	**R^2= 0.362**	R^2= 0.009	R^2= 0.186	R^2= 0.119	R^2= 0.103	R^2= 0.203	**R^2= 0.509**	**R^2= 0.839**	**R^2= 0.830**					
	p<0.0001	p= 0.5759	p= 0.0077	p= 0.0363	p= 0.0527	p= 0.0051	**p<0.0001**	**p<0.0001**	**p<0.0001**					
PFDoDA	R^2= 0.157	R^2= 0.0001	R^2= 0.071	R^2= 0.130	R^2= 0.064	R^2= 0.114	R^2= 0.208	**R^2= 0.477**	**R^2= 0.511**	**R^2= 0.554**				
	p= 0.0153	p= 0.9649	p= 0.1118	p= 0.0283	p= 0.1306	p= 0.0406	p= 0.0046	**p<0.0001**	**p<0.0001**	**p<0.0001**				
PFTrDA	R^2= 0.114	R^2= 0.001	R^2= 0.025	R^2= 0.022	R^2= 0.009	R^2= 0.040	R^2= 0.108	R^2= 0.324	R^2= 0.294	**R^2= 0.475**	R^2= 0.279			
	p= 0.0414	p= 0.8269	p= 0.3462	p= 0.3844	p= 0.5782	p= 0.2376	p= 0.0474	p= 0.0002	p= 0.0005	**p<0.0001**	p= 0.0008			
PFBS	R^2= 0.005	R^2= 0.020	R^2=0.0004	R^2= 0.092	R^2= 0.015	R^2= 0.015	R^2= 0.012	R^2= 0.0008	R^2= 1.0e-06	R^2= 0.017	R^2= 0.015	R^2= 0.005		
	p= 0.6714	p= 0.3991	p= 0.9102	p= 0.0687	p= 0.4742	p= 0.4728	p= 0.5185	p= 0.8711	p= 0.9532	p= 0.4397	p= 0.4651	p= 0.6737		
PFHpS	R^2= 0.049	R^2= 0.054	R^2= 0.003	R^2= 0.080	R^2= 0.003	R^2= 0.0001	R^2= 0.0002	R^2= 0.018	R^2= 0.042	R^2= 8.2e-06	R^2= 0.013	R^2= 0.004	R^2= 0.229	
	p= 0.1857	p= 0.1646	p= 0.7445	p= 0.0897	p= 0.7328	p= 0.9664	p= 0.9269	p= 0.4289	p= 0.2216	p= 0.9866	p= 0.4947	p= 0.6937	p= 0.0027	
PFOS	R^2= 0.104	R^2= 0.086	R^2= 0.069	R^2= 0.008	R^2= 0.043	R^2= 0.072	R^2= 0.042	R^2= 0.055	R^2= 0.070	R^2= 0.007	R^2= 0.003	R^2= 0.001	R^2= 0.312	**R^2= 0.594**
	p= 0.0513	p= 0.0781	p= 0.1151	p= 0.6042	p= 0.2173	p= 0.1095	p= 0.2251	p= 0.1637	p= 0.1132	p= 0.6339	p= 0.7302	p= 0.8563	p= 0.0003	**p<0.0001**
FOSA	R^2= 0.240	R^2= 0.160	R^2= 0.179	R^2= 0.0007	R^2= 0.025	R^2= 0.066	R^2= 0.011	R^2= 0.014	R^2= 0.027	R^2= 0.014	R^2= 0.016	R^2= 0.041	R^2= 0.049	R^2= 0.043
	p= 0.0021	p= 0.0143	p= 0.0091	p= 0.8773	p= 0.3468	p= 0.1245	p= 0.5286	p= 0.4779	p= 0.3344	p= 0.4883	p= 0.4572	p= 0.2323	p= 0.1888	p= 0.2198

From 2000 – 2002, 3M, one of the major global producers of perfluoroalkyl substances phased out the production of the synthetic precursor to FOSA and PFOS, perfluorooctane sulfonyl fluoride (POSF), as well as related products based on C6, C8, and C10 chemistry.[52,54] These were replaced with C4-based chemistry, where products were derived from perfluorobutane sulfonyl fluoride (PBSF). These compounds are believed to have lower bioaccumulative and toxicological effects.[55] Reported production of PBSF in the United States has almost doubled from 2002 to 2006, while that of POSF has decreased by more than two orders of magnitude between 1998 and 2002, with no known production after 2006.[50] Before 2003, 3M was responsible for the majority of global PFOS production.[56] By 2006, PFOS and related substances derived from POSF were regulated under the European Union (EU) Directive 2006/122/EC and by 2009, were listed under Annex B (restriction of production and use) of the Stockholm Convention on Persistent Organic Pollutants coordinated by the United Nations Environment Programme (UNEP).[49] These production changes in PFOS in the early 2000s were used to explain temporal trends in the Canadian Arctic.[57] The decline in production of the precursor FOSA by 3M is consistent with FOSA trends observed on the Devon Ice Cap, in which the majority of FOSA is <LOD after 2000, suggesting an effective phase out of this compound (Figure 3.8b). This was similarly observed in samples collected from Devon Ice Cap in 2008,[19] in North Atlantic pilot whales harvested between 1986 and 2013,[59] and in Arctic air at Alert.[60]

Temporal trends of PFOS deposition to the Devon Ice Cap do not reflect the production phase out of PFOS by 3M in the early 2000s (Figure 3.8A). Rather, PFOS

production and manufacturing, along with replacements (e.g. PFBS), have increased dramatically in Asia since 2001, and China is now the dominant producer of these compounds.[61–63] PFOS production in China began increasing rapidly around 2000 and is currently steady at 100 – 200 t yr^{-1}.[51] China was reported to be the main producer and user of POSF between 2003 – 2008 with less than 50 t in 2003 and up to 250 t of POSF-based products produced in 2008.[56] During this time, over 100 t of PFOS was also used annually in China to produce aqueous film forming foams (AFFFs),[64] used for extinguishing fuel-based fires. According to available 2006 inventories, 15 Chinese enterprises were producing over 200 t of POSF, of which 100 t were for export.[65] This suggests the annual volume of PFOS production in China in the mid-2000s was similar to the annual production by 3M in the late 1990s.[64] Although it is known that the production of perfluoroalkane sulfonyl fluorides has increased in China, global emission data for individual compounds is currently unavailable and cannot be correlated with the temporal trends observed on the Devon Ice Cap.[66] However, the continuous detection of PFOS after the early 2000s on the Devon Ice Cap may be related to the ongoing production and use of PFOS substances by manufacturers in Asia.[53] Production of other PFOS-related perfluorinated chemicals is ongoing in China, as well as in Russia and India[67] which is supported by higher levels of PFOS after 2011 in the Devon Ice Cap. An anomalously high PFOS flux was observed in 2013. This flux was between five and eight times greater than both previous and following years. There was no signal enhancement for other PFAS in 2013 and the air mass transport model showed no transport anomaly for this year. Therefore, the large 2013 PFOS flux in Devon Ice Cap is unlikely attributed to contamination during method collection or analysis, or due to air mass movements. The

reason for the high 2013 PFOS flux is unknown but may suggest other sources. Arctic air samples collected at Alert also showed the highest levels of PFOS in 2013,[68] and anomalously high PFOS levels were observed in landlocked Arctic Char from Cape Bounty, Melville Island in Nunavut, Canada, collected between 2011 – 2015.[69] This increasing PFOS trend warrants further consideration in order to determine the efficacy of current POSF restrictions.

3.3.5 PFCA Homologues and Volatile Precursors

Indirect sources of PFAAs are contributors to the global presence of these compounds, but contamination is more important for certain homologues in some locations, for example the Canadian Archipelago.[70] This has been demonstrated in multiple studies that detected the presence of volatile precursors (e.g. FTOHs, NAFSAs, NAFSEs), and FTOH-precursor degradation products (e.g. fluorotelomer unsaturated carboxylic acids (FTUCAs)), in the Canadian Arctic.[2,71–73] Volatile precursor compounds will oxidize in the atmosphere to produce PFCAs. Patterns of PFCA homologues are useful in examining the role that fluorotelomer-derived compounds play in gas-phase atmospheric oxidation.[12] If these compounds are coming from the same source, then sequential pair concentrations are expected to vary through time together. There will be some variability in the ratios depending on the relative atmospheric levels of NO_x (NO + NO_2) and peroxy radicals.[6] In this study, comparisons were made between observed concentrations of 66 pairs of PFCA homologues ranging from TFA to PFTrDA (Table 3.1). Most sequential pairs of PFCA homologues were deposited in similar amounts on the ice cap. Pairs of PFCA homologues <PFPeA had weaker correlations ($p \leq 0.0004$;

$0.308 \leq R^2 \leq 0.517$), but given the strong contribution of heat transfer fluid degradation to the fluxes of these compounds, lower correlations are expected (see Chapter 4). Correlations between sequential pairs from PFPeA and PFDoDA were all statistically significant (two-tailed t-test) with strong correlations (all p-values ≤ 0.0001; $0.527 \leq R^2 \leq 0.889$; Table 3.1). Similar correlations were observed for a number of PFCA homologues in previous ice core samples from the Devon Ice Cap[19] and the Longyearbreen glacier in Svalbard.[24] The correlations are consistent with expected PFCA homologue production via gas phase atmospheric oxidation of fluorotelomer-derived compounds.[10] Smog chamber studies show that degradation of an x:2 fluorotelomer compound (i.e. containing a perfluoroalkyl moiety corresponding to $F(CF_2)_x$), will lead to comparable yields of two PFCAs with x and x+1 carbons.[10] Flux measurement ratios were calculated for six pairs of PFCA homologues from PFPeA to PFUnDA over the time series (Figure A.2). The three major even-odd pairs expected to be formed from 6:2, 8:2, and 10:2 fluorotelomer compounds are PFHxA:PFHpA, PFOA:PFNA, and PFDA:PFUnDA, respectively. The majority (82%) of the flux ratio measurements were within a factor of two, supporting the hypothesis that these sequential, even-odd homologues are likely coming from fluorotelomer-derived sources (Figure 3.9a).[10,74] Fluorotelomer compounds of different chain lengths were industrially produced and applied to different extents. I can compare these using odd-odd PFCA homologue ratios, comparing PFNA to PFPeA, PFHpA, and PFUnDA, as products of 8:2, 4:2 and 6:2, and 10:2 fluorotelomer compounds, respectively (Figure 3.9b). The dominant homologues are PFNA and PFHpA, followed by PFPeA, then PFUnDA. This suggests that 8:2 and 6:2 fluorotelomer compounds dominate as precursors, followed by the 4:2 and 10:2 fluorotelomer compounds. This

trend is consistent with our knowledge of commercial product formulations and atmospheric measurements.[6,76,77] Despite producers moving from 8:2 to shorter-chain formulations, recent FTOH atmospheric measurements have found that the 8:2 FTOH is the dominant compound in the High European Alps.[78] Therefore, it is likely that PFCAs from PFPeA to PFUnDA on the Devon Ice Cap are derived from common emission sources due to prominent quantities of residual volatile precursors in fluoropolymer products.

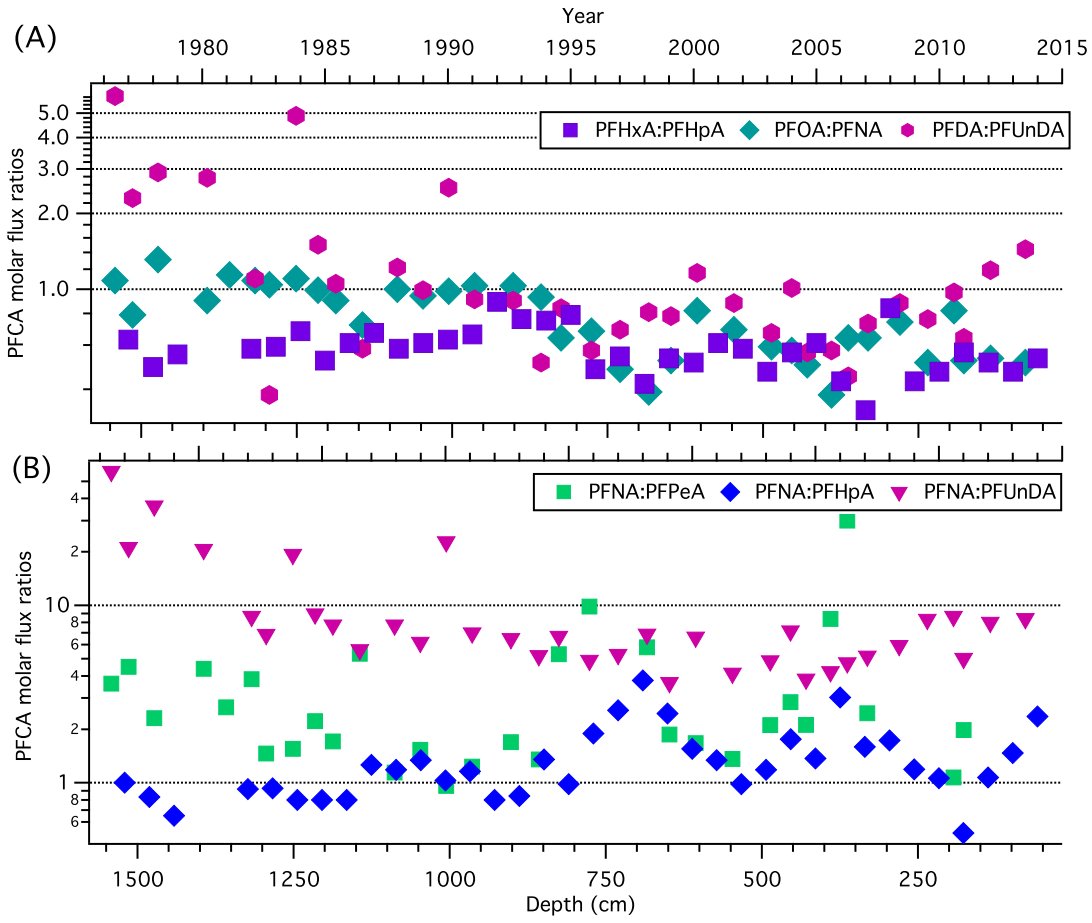

Figure 3.9. Molar flux ratios for a) three even-odd pairs of PFCAs and b) three odd pairs of PFNA with PFPeA, PFHpA, and PFUnDA homologues, as a function of depth and year.

The atmospheric oxidation of perfluoroalkane sulfonamido substances may provide an additional source of PFCAs to the Devon Ice Cap. The oxidation of FOSA could contribute to the observed flux of PFOA and short-chain PFCAs in the High Arctic. However, since there were no observed correlations between FOSA and PFOA or FOSA and any of the other PFCAs ($p \geq 0.0021$; $R^2 \leq 0.24$; Table 3.1), it is likely that PFOA deposition to the Devon Ice Cap is driven by other sources.

3.3.6 Elucidating the Role of Marine-Driven Transport of PFAAs to the Arctic

Thus far, evidence was provided for indirect formation of PFAAs in the atmosphere from volatile precursor compounds, indicating that direct transport is an unlikely source of PFAAs to the ice cap. Atmospherically formed PFAAs can deposit to any terrestrial or oceanic system, and to the atmosphere into the ocean before reaching the Arctic, and then re-enter the atmosphere from oceanic currents and marine aerosols. It is therefore important to understand the extent to which the oceans contribute to PFAA ice cap deposition. Other sources, such as dust or biomass burning, must also be considered as possible contributors of PFAAs to the ice cap. Gas-phase PFAAs will deposit through wet or dry deposition and may also be transported on aerosols.[79] Major ions are useful source markers for atmospheric aerosols, and were measured in the ice core to further understand these transport mechanisms (Tables A.7 – A.8; Figures 3.10 – 3.11).

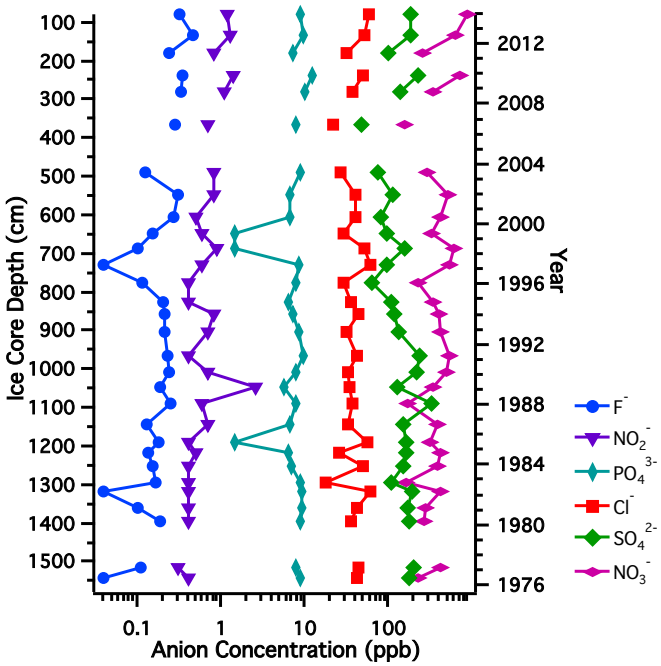

Figure 3.10. Vertical profile of anion concentrations (ng mL^{-1}) on a log scale, per depth in the ice core and by year. Anions detected include F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}.

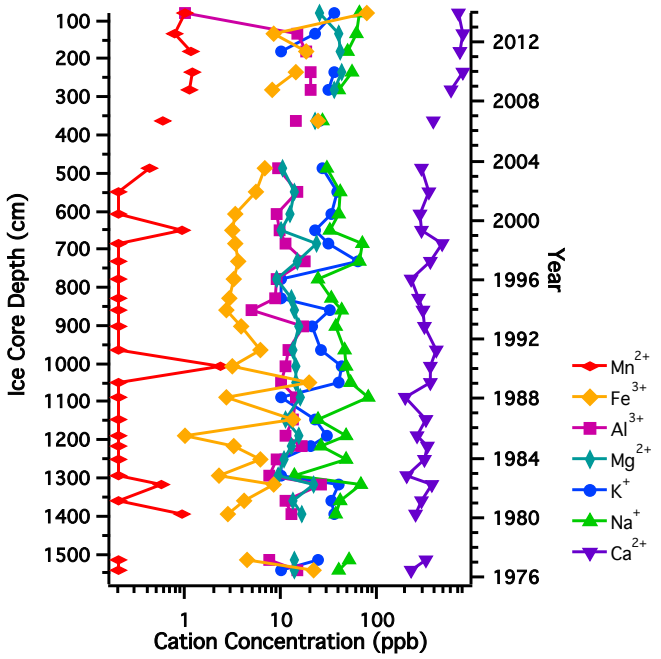

Figure 3.11. Vertical profile of cation concentrations (ng mL^{-1}) on a log scale, per depth in the ice core and by year. Cations detected include Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+} and Fe^{3+}.

The non-sea salt component of the ice core samples was calculated to understand the atmospheric origin in the samples.[24] All sodium (Na^+) in the ice core samples was assumed to come from sea salt. Most other ions were attributed to the non-sea salt component, suggesting very few oceanic sources depositing on Devon Ice Cap (Table 3.2). The non-sea salt contribution was calculated from the average molar concentration of the ions in the ice core from 1977-2015, and the average non-sea salt concentrations, which were determined by subtracting the individual ion molar concentrations from the sodium molar concentration multiplied by the expected ion to sodium ratio.[80] Further, no correlations were observed between Na^+ flux and any of the PFAAs ($p \geq 0.0093$; $R^2 \leq 0.218$; Table A.9).

Table 3.2. Non-sea salt and sea salt component concentrations (conc.) (µmol L^{-1}) of select ions in the ice core.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	F^-
Average molar conc. in ice core (µmol/L)	1.94	0.68	0.74	9.45	10.73	1.54	0.0103
Non-sea salt conc. (µmol/L)		0.64	0.52	9.41	8.39	1.42	0.0100
Sea salt conc. (µmol/L)		0.04	0.22	0.04	2.33	0.12	0.0003
Contribution of non-sea salt (%)		93.8	70.3	99.5	78.2	92.4	97.2

Another technique used to assess the influence of marine aerosol deposition of PFAAs to the Devon Ice Cap is a comparison between ocean and ice cap homologue patterns. If marine aerosols were/are a major source of PFAA contamination on Devon Ice Cap, then one would expect the homologue profiles to be similar between the ocean and the ice cap. Figure 3.12 illustrates the proportional analysis of the molar concentration (pmol L^{-1}) fraction between PFAAs on the Devon Ice Cap and ocean levels in the Canadian Artic Archipelago,[5] Arctic Ocean,[5,81] North Atlantic Ocean,[82] and North Pacific Ocean[81] for the years 2005 and 2010. Molar concentrations of PFAAs on the ice

cap differed from ocean PFAA concentrations, with higher molar concentrations of PFBA and PFNA, and lower molar concentrations of PFSAs found on Devon Ice Cap. PFHxS was not detected on the ice cap, but was measured in most ocean samples, suggesting that indirect sources are of importance for Arctic deposition, due to the absence of PFHxS on the ice cap.[19] The differences in homologue profiles between the ice cap and the ocean can also not be accounted for by different surfactant properties,[19] suggesting the two may have different sources of PFAA contamination. The discrepancies between the Na^+/PFAA flux ratios and the ice cap/ocean proportional analysis provide further evidence to imply that marine aerosols are not a significant source of PFAAs to the Devon Ice Cap.

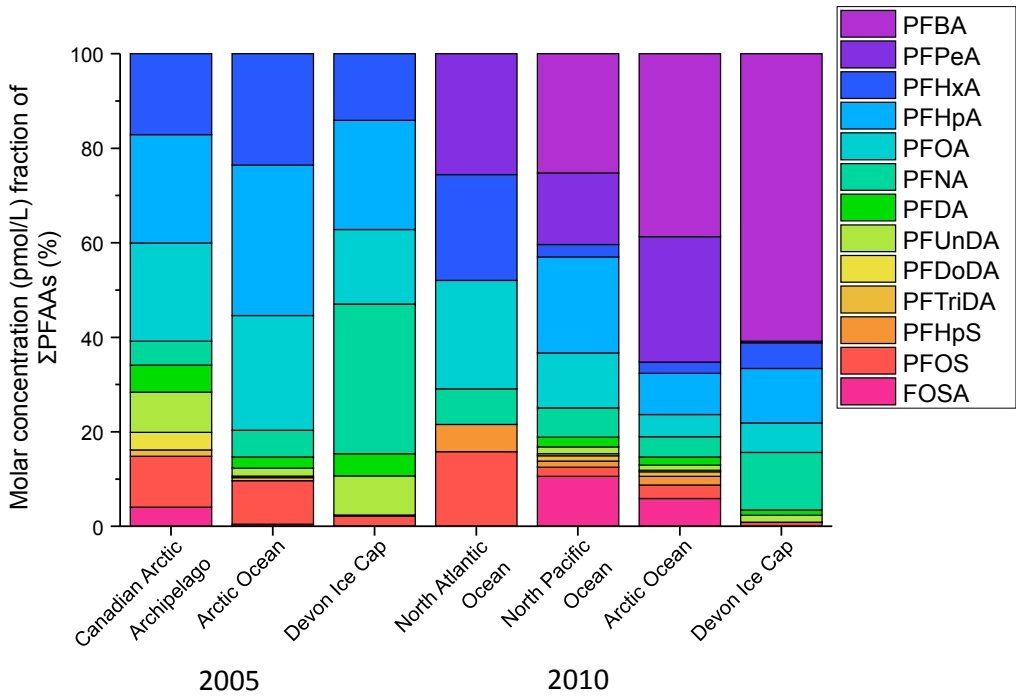

Figure 3.12. Molar concentration fraction of sum of PFAAs on the Devon Ice Cap compared to levels in the Canadian Artic Archipelago,[5] Arctic Ocean,[5,81] North Atlantic Ocean,[82] and North Pacific Ocean[81] in 2005 and 2010. Ocean concentrations are compared to ice cap concentrations for two years to show a better overall comparison with different ocean samples that were collected in multiple field campaigns.

3.3.7 Understanding Atmospheric Inputs of PFAAs Using Ion Tracers

Weak correlations were observed between short-chain PFCAs and nss-F^- ($p \leq 0.0015$; $0.306 \leq R^2 \leq 0.455$). A small percentage of the F^- being detected in the ice core samples may be derived from the atmospheric formation of PFCAs. The degradation of many PFCA precursors, including heat transfer fluids, forms both PFCA and HF. For example, the hydrolysis of perfluoroacyl fluorides forms the corresponding PFCAs along with the loss of HF[83]:

$$CF_3(CF_2)_xCOF + H_2O \rightarrow CF_3(CF_2)_xCOOH + HF$$

By this mechanism, PFCAs could account for between 0.80 – 14% of the F^- present on the ice cap, depending on the year. These numbers are upper limits as PFCAs can also be formed by mechanisms that do not form HF.[6] It is difficult to assess the exact contribution of this anthropogenic source to the overall burden of F^-, due to the lack of available data on F^- sources. This is further confounded by the high mobility of F^- in both firn and ice layers, which makes it difficult to study temporal trends in F^- deposition.[84] Both natural and anthropogenic sources contribute to the overall budget of F^- in the troposphere, including primary sea-salt, soil dust aerosols, volcanic emissions, coal burning, and industrial processing.[84] I am currently unable to assess the exact contributions of each source of F^-, but the correlations observed here suggest that short-chain PFCA precursor degradation could account for up to 14% of the observed F^-. Furthermore, these correlations lend further support to indirect formation as a major pathway to PFCA contamination on the Devon Ice Cap.

There were weak to moderate correlations between several PFAAs and nss-Ca^{2+} and nss-Mg^{2+} ($0.300 \leq R^2 \leq 0.531$; Table A.9), both of which are indicators of mineral dust.[85] Mineral dust aerosols can accumulate acidic atmospheric contaminants, such as nitric and hydrochloric acids, and undergo LRT during dust storms, where they can travel long distances from Asian and African dust sources to the remote Arctic.[86,87] Dust entrainment in deserts is one of the most important sources of mineral dust in the global atmosphere and North African (e.g. Sahara) and Central Asian (e.g. Gobi desert) dust sources contribute the most global dust to the Northern Hemisphere.[88] Several studies have found dust particles associated with LRT in snow and ice samples from the Canadian Arctic.[89–91] Dust deposition to the Arctic shows a seasonal effect, with dust storms in major deserts occurring more frequently in the spring, leading to higher concentrations of mineral dust tracers in the spring and autumn.[92] I detected high concentrations (199 – 786 μg L^{-1}) of Ca^{2+} on Devon Ice Cap, and calculated that the majority (99.5%) of Ca^{2+} contributed to the nss component. Substantial concentrations (<2.00 – 78.3 μg L^{-1}) of other mineral dust (Al^{3+}, Fe^{3+}, Si^{4+}) tracers were also detected. Correlations between nss-Ca^{2+} and PFAAs suggest there is a relationship between the transport of mineral dust and PFAAs to the Devon Ice Cap. This could be caused by both mineral dust and PFAAs originating from the same regions. Alternatively, it could indicate a mechanistic relationship. Atmospheric acids are known to interact with mineral dust through reactive uptake.[87] It is possible that PFAAs, as strong atmospheric acids, could behave in the same way and be taken up onto mineral dust aerosols and subsequently transported to the Arctic. I cannot distinguish between these mechanisms at

this time, and suggest that further studies explore this relationship between mineral dust and PFAA LRT.

3.4 Conclusions

Monitoring of temporal trends in persistent organic pollutant deposition in remote areas is an important initiative to determine the impact of regulation on contamination of pristine environments. This study demonstrates the value of ice cores to understanding contaminant LRT and this chapter discusses the first multi-decadal record of long-chain PFAA deposition in the Canadian Arctic. Continuous and increasing deposition of many PFAAs on Devon Ice Cap was observed, suggesting on-going emission and use of these compounds, their precursors and likely new unidentified compounds. These results indicate that Devon Ice Cap is likely impacted by global pollutants from both North American and Eurasian Sources, with Continental Asia becoming a greater contributor in recent years. Use of major ion tracers provided new information regarding the transport of PFAAs, confirming that marine aerosol inputs are unimportant and suggesting a relationship with mineral dust. I also observed that a small percentage of fluoride detected in the Arctic could be coming from the reactive mechanisms forming the PFAAs. Further efforts are necessary to continue monitoring the long-range transport of PFAAs and their deposition to the remote Canadian Arctic. It is important to understand these LRT mechanisms and determine the geographical sources of PFAAs and their precursors. Ice cores can aid in elucidating these mechanisms and further collection and analysis of ice cores is recommended.

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4 Persistent Fluorinated Compounds Increasing in the Arctic as a Result of the Montreal Protocol

4.1 Introduction

Perfluoroalkyl carboxylic acids (PFCAs) are characterized by resistance to environmental degradation and potential adverse impacts on human and environmental health,[1] each a hallmark of persistent organic pollutants. Widely used in surfactant and polymer products since the 1960s, PFCAs are accumulating in the global environment, including remote regions such as the Arctic.[2] Short-chain PFCAs with four or fewer carbons (scPFCAs, $CF_3(CF_2)_xCOOH$, $x \leq 2$) are a concern because of their toxicity to plants, and potential for accumulation in aquatic ecosystems.[3,4] Atmospheric transformation and subsequent deposition of fluoropolymer-related precursors represents a minor environmental source of scPFCAs.[5] However, an additional source from atmospheric degradation of chlorofluorocarbon (CFC)-replacement compounds is possible from known chemistry. Here, I provide the first multi-decadal temporal record of scPFCA deposition, derived from an Arctic ice core. These results bring to the forefront a need for a holistic approach to environmental risk assessment that considers impacts of replacement substances and degradation products.

4.2 Methods

The extraction and analysis of scPFCAs are based on earlier studies [[5]] with further details on sample collection, preparation, extraction and analysis in Chapter 2 – Methodology. For the scPFCA analysis, isotopically labeled (^{13}C) PFBA was used as a

surrogate standard to correct for recovery (M4PFBA) and matrix effects (M3PFBA). Due to lack of available isotopically labeled TFA and PFPrA, the closest chain length surrogate, M4PFBA was used to quantify TFA and PFPrA based on relative response using a calibration curve comprised of 15 levels of analyte (state range) and a constant level of M4PFBA. Method recoveries for the scPFCAs corresponded to 22% ± 1 for TFA, 32% ± 5 for PFPrA, and 107% ± 16 for PFBA based on comparing the peak area in the pre-extraction spike to the post-extraction spike, n=3. Though these recoveries are lower than 50% for TFA and PFPrA, they are consistent and the recovered TFA and PFPrA in actual samples were well above the limits of quantification. Slight matrix suppression was noted for scPFCAs by comparing the post-extraction sample spike to a solvent spike. Matrix effects corresponded to −17% ± 1 for TFA, −19% ± 3 for PFPrA and −25% ± 6 for PFBA. Sample concentrations were recovery and matrix effect corrected by using relative responses to M3PFBA. LC-MS/MS chromatograms for the standards, method blanks and ice core samples are provided in Appendix B.

4.3 Results and Discussion

Fluoropolymer and related precursors, such as fluorotelomer alcohols ($F(CF_2CF_2)_nCH_2CH_2OH$) produce PFCAs as minor products, whereas CFC-replacement compounds produce scPFCAs as both major (molar yield > 0.1) and minor (molar yield < 0.1) products.[6] The fractional molar yield (i.e. percent yield) corresponds to how much of the scPFCAs (e.g. ~1 or ~100%) can be produced from the degradation of the corresponding precursors. Three scPFCAs can be formed: trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), and perfluorobutanoic acid (PFBA). Major and minor

precursor sources (Table 4.1) include hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), other halogenated ethanes and ethers, hydrofluoroethers (HFEs), hydrofluoroolefins (HFOs), and perfluoroolefins (PFOs).

Table 4.1. Major and minor precursor sources for short-chain PFCAs.

	Commercial compound	Chemical formula	Atmospheric lifetime (years)[a]	Fractional Molar Yield[b]		
				TFA	PFPrA	PFBA
Major Precursors	Halothane (Halon-2311)	$CF_3CHClBr$	1.0	~1[7]		
	HCFC-123	CF_3CHCl_2	1.3	0.98[8]		
	HCFC-124	CF_3CHFCl	5.9	~1[8]		
	HCFC-133a	CF_3ClCH_2	4.0	>0.5[9]		
	HCFC-225ca	$CF_3CF_2CHCl_2$	1.9		~1[10]	
	HFC-134a	CF_3CH_2F	14	~0.17[11]		
	HFC-227ea	CF_3CHFCF_3	38.9	0.94 ± 0.06[12]		
	HFC-245eb	CF_3CHFCH_2F	3.2	Unknown		
	HFC-236ea	$CF_3CHFCHF_2$	11.0	Unknown		
	HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	16.1	Unknown	Unknown	
	HFO-1234yf	$CF_3CF=CH_2$	10.5 days	~1[13]		
	HFO-1225ye (E)	$CF_3CF=CHF$-(*E*)	4.9 days	~1[14]		
	HFO-1225ye (Z)	$CF_3CF=CHF$-(*Z*)	8.5 days	~1[14]		
	PFO-1216	$CF_3CF=CF_2$	4.9 days	~1[15]		
	HFE-236ea2 (Desflurane)	$CHF_2OCHFCF_3$	10.8	Unknown		
	HCFE-235da2 (Isoflurane)	$CF_3CHClOCHF_2$	3.5	0.95 ± 0.03[16]		
Minor Precursors[c]	HFC-125	CF_3CHF_2	31.0	<0.1		
	HFC-143a	CF_3CH_3	51.0	<0.1		
	HFC-329p	$CF_3CF_2CF_2CHF_2$	33.0	<0.1	<0.1	<0.1
	HFC-236cb	$CF_3CF_2CH_2F$	13.0		<0.1	
	HFE-143a	CF_3OCH_3	4.8	<0.1		
	HFE-245cb2	$CF_3CF_2OCH_3$	5.0	<0.1	<0.1	
	HFE-7100	$CF_3(CF_2)_3OCH_3$	4.7	<0.1	<0.1	<0.1
	HFE-7200	$CF_3(CF_2)_3OCH_2CH_3$	0.80	<0.1	<0.1	<0.1
	Polymer Precursors		~1-170 days	<0.1	<0.1	<0.1

[a]All major precursor lifetimes are from [17] and references therein.
[b]Yields are based on either experimental data or recommended data. Major precursors have fractional molar yields > 0.1 and minor precursor yields are < 0.1.
[c]All minor precursor yields are from [6] and references therein.

Measurements of PFCAs in high-elevation Arctic ice caps indicate that long-range atmospheric transport is occurring.[5] As strong organic acids[6] PFCAs are removed from the atmosphere to the surface via dry deposition or cloud droplet scavenging and wet deposition, resulting in lifetimes of hours to days after atmospheric formation.[18,19] Atmosphere-surface flux measurements of scPFCAs that could elucidate sources and transport pathways are rare.[20–22] In this study, a 15.5-m ice core was collected from the summit of Devon Ice Cap, Nunavut (75.2°N, 82.7°W, 2175 m above sea level) in May 2015, representing 37 prior years of deposition. An age-depth scale was created using oxygen stable isotopes and ion chemistry measured in a co-located core. The ice core was sectioned and analyzed for PFCAs, and a long-term atmospheric deposition record was generated.

Observed scPFCA fluxes in the Devon Ice Cap range from <5.3 to 44,420 ng m^{-2} yr^{-1}. Similar fluxes of TFA, PFPrA, and PFBA were measured in precipitation samples collected in North America and Japan between 1998-2002[20] and 2006-2008,[21] respectively. These studies do not provide continuous temporal data and represent semi-quantitative estimates of total deposition flux. Modelling studies conducted in the 1990s examined the potential impact of HCFC and HFC introduction on TFA deposition. Cumulative northern hemisphere TFA deposition was predicted over the periods 1985-2010[18] and 1990-2020[19] to be 500 μg m^{-2} and 342 μg m^{-2}, respectively. These are comparable to our observations of cumulative TFA deposition during the same time frames (1985-2010: 276 μg m^{-2}; 1990-2014: 349 μg m^{-2}), suggesting that such replacements represent major sources of global scPFCA contamination.

CFCs are known stratospheric ozone-depleting substances (ODSs) that are regulated by the Montreal Protocol. This international agreement entered into force in 1989 and mandated replacement of ozone-depleting CFCs with HCFCs, HFCs, and other substances with lower ozone depleting potentials by 2010.[23] From 1990-1999, several amendments were made to the Montreal Protocol to regulate HCFCs, with complete phase out by 2020 or 2030 for developed and developing countries, respectively.[24] The 2016 Kigali Amendment proposed a phase-down of HFCs with a production freeze in 2024 and an 80% reduction by 2043 in developed countries, with a similar strategy in developing countries.[23] The Montreal Protocol has unequivocally reduced the impact of ODSs on the stratospheric ozone layer.[17] Many ODSs are also long-lived greenhouse gases and thus the Montreal Protocol concurrently decreased anthropogenic radiative forcing.[17] Despite these clear benefits, increased production and consumption of CFC-replacement compounds increases the environmental burden of scPFCAs. Current environmental scPFCA levels are not sufficient to cause known ecotoxicological effects;[4] however, scPFCAs are environmentally persistent and will continue to accumulate so long as precursors are in use.

Temporal trend analysis using an ice core can elucidate various source and precursor contributions to long-range transport of scPFCAs. From ~1977 to ~1989 scPFCAs were consistently detected at low levels (Figure 4.1A) in the Devon Ice Cap record. I represent ice core temporal trends as 5-year moving averages of annual data to reduce the influence of dating errors (±1 year) and possible melting effects (± 1 year).[5] Starting in ~1990 fluxes of TFA, PFPrA, and PFBA increase coincidentally with the

known introduction and emissions of CFC-replacement compounds. In contrast, no increase is observed for perfluorohexanoic acid (PFHxA), which cannot be formed from the degradation of CFC-replacement compounds. Atmospheric lifetimes of CFC-replacement precursors are sufficiently long (Table 4.1) that they are well mixed in the northern hemispheric troposphere. Therefore, long-term temporal trends in deposition should reflect historic changes in global production and emissions

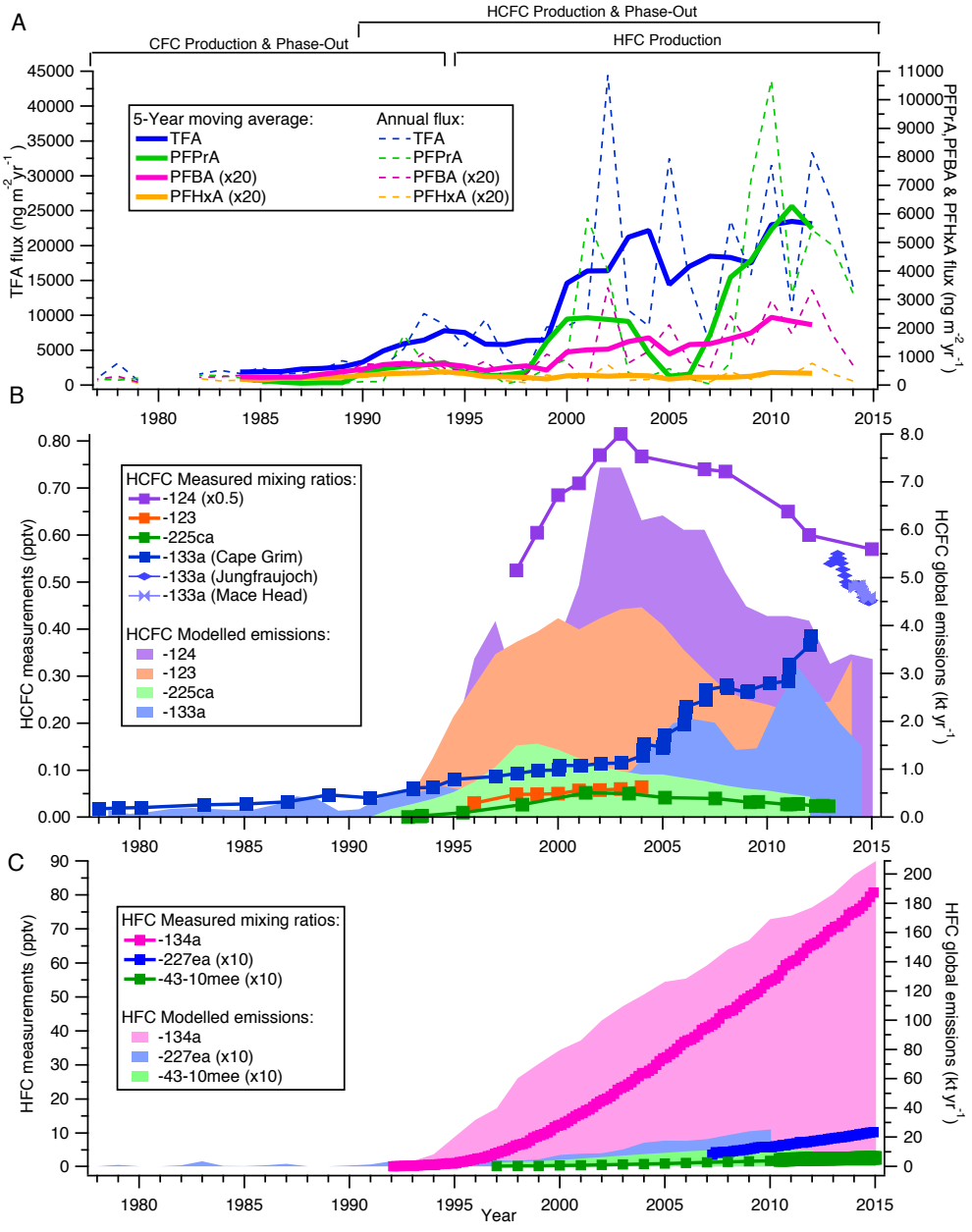

Figure 4.1. A) Annual scPFCA deposition fluxes and 5-year moving averages. B) HCFC atmospheric measurements (HCFC-124: measured mean mixing ratios from Mace Head, Ireland (MH) and Cape Grim, Tasmania (CG);[25] HCFC-123: measured mean mixing ratios from CG;[25] HCFC-225ca: mixing ratios from CG; HCFC-133a: mixing ratios from CG, Jungfraujoch, Switzerland (JF), and MH[26]) and global modelled emissions.[27–29] (C) HFC atmospheric measurements (HFC-134a and HFC-227 global mixing ratios;[30] HFC-43-10mee averaged mixing ratios for Northern Hemisphere sites: Trinidad Head, California; Zeppelinfjellet, Svalbard; JF; and MH[31]) and global modelled emissions.[25]

Use of CFC-replacement compounds was minimal prior to enactment of the Montreal Protocol (~1990) when the primary atmospheric anthropogenic source of scPFCAs was degradation of fluoropolymers and related precursors.[3,32] Rapid growth in production—and release through use—of HCFCs, came with global adoption of Montreal Protocol regulations. There are four known HCFCs that produce TFA and PFPrA as major products (Table 4.1). Large-scale use of these HCFC precursors began ~1990, coincident with observed increases of TFA and PFPrA on the ice cap (Figure 4.1B).[25,27–29] Production of HFCs has been increasing steadily since 1995 in developed countries. China emerged as a major HFC producer and consumer in the early 2000s.[33] Several HFCs produce TFA and PFPrA as major and minor products and a few will additionally produce PFBA as a minor product. Atmospheric measurements and modelled global emission data are available for three major HFC precursors to scPFCAs (Figure 4.1C),[25,31,30] which increased in the early 1990s. Temporal trends in the measured Arctic ice core scPFCA fluxes are consistent with production and emissions of CFC-replacement precursors (Figure 4.2). Based on production volume, the dominant precursor for TFA is HFC-134a, which is the CFC-12 substitute used in mobile air conditioning.[30] Summed emissions of precursors increased in the early 1990s, including HFC-134a, HCFCs, and volatile anaesthetics. The observed flux of TFA in the ice core record began increasing 2-3 years earlier (~1990) and continues to increase in the core to present day (Figure 4.2A). Mixing ratios of TFA precursors correlate strongly and significantly with increasing TFA deposition on Devon Ice Cap ($r^2 = 0.758$, $p < 0.0001$).

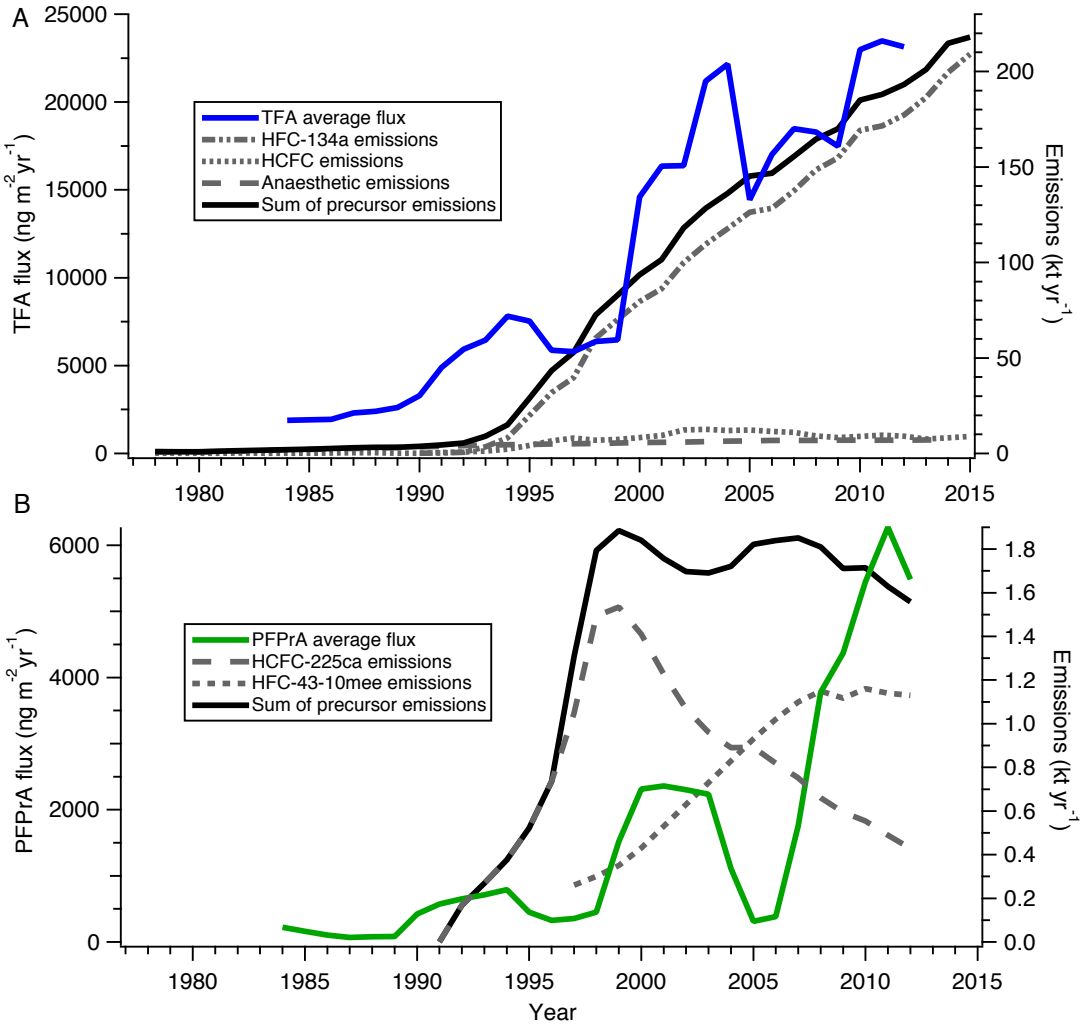

Figure 4.2. Temporal trends of CFC-replacement precursor emissions and TFA and PFPrA deposition fluxes. (A) HFC-134a,[25] sum of HCFC (HCFC-123, -124, -133a)[28,29] and sum of anaesthetic emissions (halothane and desflurane),[34] compared to 5-year average TFA flux on Devon Ice Cap over time. (B) HCFC-225ca[27] and HFC-43-10mee[25] emissions, compared to 5-year average PFPrA flux on Devon Ice Cap over time.

Two compounds that produce PFPrA as a major product have emission data available: HCFC-225ca and HFC-43-10mee. HCFC-225ca was introduced in the early 1990s, with peak modelled emissions (1.51 kt yr^{-1}) in 1999, followed by a decline in accordance with the Copenhagen (1992) and Vienna (1995) Amendments to the Montreal

Protocol.[27] HFC-43-10mee was introduced in the mid-1990s, with increasing emissions until 2012 (1.13 ± 0.31 kt yr^{-1}).[31] These PFPrA precursor emissions match well with the increase in its deposition flux around 2000, coincident with the peak emissions of HCFC-225ca (Figure 4.2B). Another increase in PFPrA flux is observed after 2005, corresponding with increasing emissions of HFC-43-10mee. Mixing ratios of PFPrA precursors show moderate and significant correlation with increasing PFPrA deposition ($r^2 = 0.678$, $p < 0.0001$). Temporal trends of TFA and PFPrA fluxes coinciding with modelled emissions of these major precursors implicates known atmospheric degradation of CFC-replacement precursors regulated and released by amendments to the Montreal Protocol as the source of this contamination.

With continued regulation of CFC-replacement compounds—most recently the 2016 Kigali Amendment—there will be further impacts on the regional environmental burden of scPFCAs near emission sources. A major replacement class for HFCs is HFOs, which have shorter atmospheric lifetimes (<1 month), and thus will not become well mixed in the troposphere. Production of scPFCAs from HFOs occurs in yields close to 100%[35] (Table 4.1), which will result in downwind environmental contamination. HFO-1234yf is being positioned as the next-generation mobile air conditioning refrigerant to replace HFC-134a,[36] with North American production estimates of 50-100 kt yr^{-1} for the next 50-100 years.[4] HFO-1234yf produces TFA in 100% molar yield.[35,37] Implementation of HFO-1234yf as the major replacement for HFC-134a has been estimated to result in annual TFA wet deposition of 160-240 μg m^{-2} in continental North America,[38] comparable to the cumulative ice core deposition during the decade from 2005 to 2014

(208 μg m^{-2}). The short atmospheric lifetimes of HFOs means their impact on scPFCA deposition will be spatially variable, resulting in higher regional contamination downwind of source regions, followed by global dissemination of the persistent products. HFO-1234yf has recently been detected at low levels in a populated area,[36] but the magnitude of its presence in the High Arctic has not yet been reported. By shifting from HFC-134a to HFO-1234yf production, the environmental TFA burden will likely increase. Because of the persistence and high environmental mobility of TFA, this will result in further TFA contamination of aquatic systems including wetlands[39] and oceans.[3]

4.4 Conclusions

These ice core measurements provide evidence that elevated scPFCA depositional fluxes to the High Arctic are driven primarily by increased emissions of volatile CFC-replacement compounds introduced because of the Montreal Protocol. Prior to the Montreal Protocol, total northern hemisphere deposition of scPFCAs was less than 450 kt annually. In recent years, this has increased ten-fold to almost 4500 kt per year. These scPFCAs have no known environmental degradation pathway and therefore will accumulate in the environment while precursors continue to be emitted. The Montreal Protocol will undoubtedly continue to positively impact stratospheric ozone and climate and represents an unparalleled achievement in global environmental stewardship. However, this study emphasizes that even the most successful regulations can result in unintended environmental impacts. Replacement of one class of performance chemicals with another can lead to different, often unanticipated, environmental effects that persist for the foreseeable future. These findings exemplify the continued need for holistic

consideration of replacement substances – for example, identification of environmental degradation products before use – in assessing regulatory efficacy.

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5 Conclusions and Future Directions

This work has demonstrated three major points: the unique and valuable use of ice cores in understanding long-range transport (LRT) of perfluoroalkyl acids (PFAAs); the continuous and increased deposition of PFAAs to the remote Canadian Arctic; and the elevated fluxes of short-chain perfluoroalkyl carboxylic acids (scPFCAs) as a result of regulations implemented by The Montreal Protocol.

The 15.5 m ice core collected from Devon Ice Cap in the Canadian Arctic has provided an invaluable record of past atmospheric pollution. Not only did I detect a wide range of PFAA analytes in the ice core, but I was able to create the first multi-decadal temporal ice record in PFAA deposition. This long-term archive provided me with useful data that allowed me to determine production changes, pollutant sources and transport pathways of these PFAA contaminants over time.

In this work I observed ongoing and in some cases, increased deposition of PFAAs on Devon Ice Cap. This suggests that there is ongoing emissions and use of these compounds, their precursors and likely new unidentified compounds. I correlated PFAA homologues in further understanding the role that precursor compounds play in LRT. I determined that the majority of the PFCAs are likely derived from common emission sources due to prominent quantities of residual volatile precursors in fluoropolymer products, which are then degrading in the atmosphere and depositing to the Arctic. Additionally, I compared these ice core measurements to all other studies, regulations, and voluntary reductions, to further understand these emission sources. I found that

regulations including the US EPA PFOA Stewardship Program, and the Canadian Environmental Performance Agreement, in addition to the 3M phase-out, have in turn led to new manufacturers, largely in Continental Asia, beginning to produce these PFAAs and their precursors. This was similarly observed for the scPFCAs, which were detected at elevated fluxes due The Montreal Protocol and its Amendments, which have regulated the phase-out of CFC-compounds with replacements including the HCFCs, HFCs, HFEs, and HFOs, that degrade to scPFCAs in the atmosphere. My work demonstrates that even successful regulations can lead to effects of environmental concern, and highlights a need to consider the holistic nature of environmental processes and impacts.

In this work I performed air mass transport modelling to determine the source regions of these global pollutants, and found that Devon Ice Cap is indeed impacted by air masses from both North America and Eurasia. This further confirmed my proposal that new manufacturers in Continental Asia are contributors to PFAAs deposited on Devon Ice Cap. Furthermore, I conducted major ion analyses to determine if major ion tracers could provide me with any new information regarding PFAA transport. Based on correlations with the Na^+ tracer and the proportional analysis between ice cap and ocean PFAA concentrations, I discovered that marine aerosol transport does not play a significant role in PFAA deposition. Mineral dust is likely an important contributor, based on mineral dust tracers, including Ca^{2+}. This is also one of the first studies to provide evidence to suggest that a small percentage of the F^- detected in the Arctic could be coming from the PFAAs themselves, based on atmospheric precursor degradation mechanisms.

Overall, assessments of deposition, homologue profiles, ion tracers, transport models, and production and regulation trends have improved current understandings of LRT of PFAAs to Devon Ice Cap. Further efforts are necessary to continue monitoring the LRT of these contaminants, their precursors, and replacement compounds, that will continue to lead to elevated levels of these persistent pollutants in the remote Canadian Arctic. Due to the invaluable information that ice core records can provide, and with increased analytical capabilities today, future work needs to involve analyzing more contaminants, at lower detection limits, in single ice cores.

Appendix A – Supporting Information for Chapter 3

Table A.1. Depth profile (cm) of PFCA concentrations (pg L^{-1}) on the Devon Ice Cap. Values <LOD are in red and values <LOQ are in blue. All samples are <LOQ for PFTeDA, PFHxDA and PFOcDA and are not shown here.

		Concentration (pg L^{-1})											
Depth (cm)	Year	TFA	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA
19	2015	38194	12977	245	<10.4	43.0	55.0	102	140	17.0	<15.7	<3.61	<3.21
78	2014	87558	19993	215	<10.4	42.8	94.4	129	284	54.0	41.1	<3.61	<3.21
134	2013	126723	23788	429	<10.4	95.2	235	207	440	72.3	66.8	<3.61	<3.21
177	2012	168508	27472	844	<10.4	193	438	275	596	84.2	145	<12.0	<3.21
193	2011	159006	47679	1339	<10.4	280	578	278	382	47.6	53.8	<3.61	<3.21
235	2010	208497	70572	984	<10.4	130	317	195	427	43.0	62.4	<3.61	<3.21
280	2009	96011	43576	409	<10.4	63.7	173	173	262	43.3	53.8	<3.61	<3.21
331	2008	104351	3460	536	73.8	104	144	181	319	49.8	75.2	<3.61	<3.21
363	2007	40983	<514	202	<10.4	38.7	135	156	274	29.0	70.1	<3.61	<3.21
390	2006	122894	1862	335	51.3	73.4	196	258	755	113	218	<12.0	4.96
429	2005	198378	3534	646	108	122	231	180	403	65.6	128	<5.12	<3.21
454	2004	81858	2845	575	88.8	94.9	198	226	443	69.2	75.4	<3.61	<3.21
487	2003	99102	3923	356	74.0	73.5	183	144	274	41.7	68.6	<3.61	<3.25
547	2002	150890	13667	581	126	120	241	185	302	70.8	88.6	5.71	<3.21
606	2001	38736	22990	<39.8	54.2	48.9	93.1	116	159	31.0	29.3	<3.61	<3.21
648	2000	46958	5081	222	92.9	68.3	155	142	306	72.5	102	<3.61	<3.21
684	1999	37737	2679	245	54.5	80.8	178	195	555	72.6	98.1	6.84	<3.21
730	1998	14273	1396	145	<10.4	29.2	80.1	166	385	56.0	88.7	<3.61	<3.21
776	1997	20590	801	<133	<34.7	42.7	91.9	181	299	38.8	74.4	<3.61	<3.21
825	1996	38902	2119	174	62.9	101	243	333	584	81.8	106	<3.61	<3.21
857	1995	37254	2841	165	95.0	122	180	186	225	24.2	52.6	<3.61	<3.21
902	1994	41004	2176	141	81.0	90.8	140	221	241	37.1	45.2	<3.61	<3.21
964	1993	33936	2681	187	79.9	107	162	159	173	24.9	30.2	<3.61	<3.21
1006	1992	26591	9017	165	87.1	112	145	129	147	18.1	<15.7	<3.61	<3.21
1047	1991	13202	595	177	79.4	82.0	145	178	213	37.8	41.9	<3.61	<3.21
1088	1990	14420	591	186	81.4	67.5	124	145	163	28.5	25.7	<3.61	<3.21
1144	1989	12599	<514	<133	<34.7	49.7	95.1	105	162	18.7	35.2	<3.61	<3.21
1187	1988	9962	<514	<133	87.1	87.1	174	209	262	39.4	41.2	<3.61	<3.21
1216	1987	11457	<514	<133	35.4	50.0	86.5	122	138	25.8	18.9	<3.61	<3.21
1251	1986	7819	570	<133	46.1	65.2	124	122	125	35.0	<15.7	<3.61	<3.21
1294	1985	11652	<514	<133	39.2	44.2	98.3	93.8	101	<12.5	17.9	<3.61	<3.21
1317	1984	12999	2015	133	<34.7	67.1	115	112	117	16.4	16.4	<3.61	<3.21
1358	1983	9687	1521	<133	<34.7	34.6	68.1	82.2	81.0	<12.5	<4.72	<3.61	<3.21
1394	1982	7716	1682	<133	<34.7	56.2	113	107	133	19.9	<15.7	<3.61	<3.21
1420	1981												
1458	1980												
1473	1979	8383	3069	<133	<34.7	40.4	85.5	82.5	70.4	<12.5	<4.72	<3.61	<3.21
1514	1978	13339	735	<133	<34.7	54.8	130	96.6	137	16.5	<15.7	<3.61	<3.21
1542	1977	6555	1462	<133	<34.7	47.2	86.7	107	110	12.6	<4.72	<3.61	<3.21

Table A.2. Depth profile (cm) of PFSA concentrations (pg L^{-1}) on the Devon Ice Cap. Values <LOD are identified in red. All samples are <LOD for PFHxS, PFDS and PFECHS and are therefore not shown here. No values are provided for the years 1980 – 1981, as there were no ice core samples available for those two years.

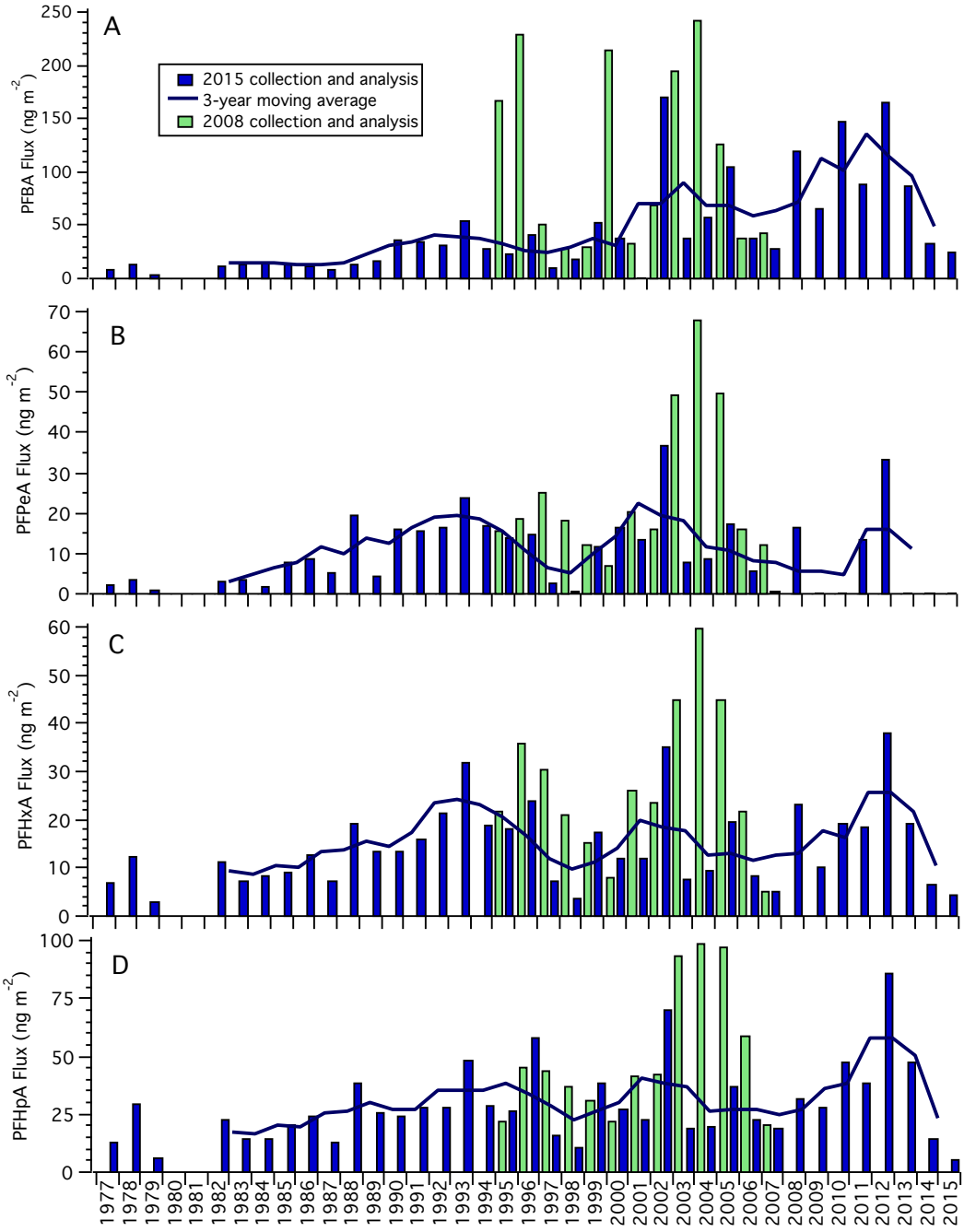
		Concentration (pg L^{-1})			
Depth (cm)	Year	PFBS	PFHpS	PFOS	FOSA
19	2015	6.80	<1.43	52.2	<0.18
78	2014	<3.62	9.28	94.8	<0.18
134	2013	4.19	8.77	391	<0.18
177	2012	<3.62	<1.43	50.8	1.50
193	2011	<3.62	<1.43	103	<0.18
235	2010	<3.62	<1.43	32.0	<0.18
280	2009	<3.62	<1.43	27.8	<0.18
331	2008	<3.62	<1.43	30.5	<0.18
363	2007	<3.62	<1.43	21.9	<0.18
390	2006	<3.62	<1.43	29.8	<0.18
429	2005	<3.62	<1.43	29.0	1.69
454	2004	<3.62	<1.43	32.7	<0.18
487	2003	<3.62	<1.43	24.8	7.00
547	2002	<3.62	<1.43	32.5	<0.18
606	2001	<3.62	<1.43	11.9	<0.18
648	2000	<3.62	<1.43	24.6	1.48
684	1999	<3.62	<1.43	21.5	13.2
730	1998	<3.62	<1.43	37.5	71.9
776	1997	<3.62	<1.43	17.8	43.6
825	1996	<3.62	<1.43	19.7	41.9
857	1995	<3.62	<1.43	29.5	41.2
902	1994	<3.62	<1.43	35.7	76.8
964	1993	<3.62	<1.43	20.2	29.7
1006	1992	<3.62	<1.43	26.6	24.5
1047	1991	<3.62	<1.43	26.6	37.5
1088	1990	<3.62	<1.43	13.7	26.6
1144	1989	<3.62	<1.43	21.7	33.1
1187	1988	<3.62	<1.43	15.9	30.2
1216	1987	<3.62	<1.43	22.8	22.2
1251	1986	<3.62	<1.43	19.8	25.0
1294	1985	<3.62	<1.43	16.9	27.9
1317	1984	<3.62	<1.43	50.3	13.6
1358	1983	<3.62	<1.43	18.7	3.72
1394	1982	<3.62	<1.43	22.6	14.8
1420	1981				
1458	1980				
1473	1979	<3.62	<1.43	15.8	<0.18
1514	1978	<3.62	<1.43	14.8	13.7
1542	1977	<3.62	<1.43	13.8	10.2

Table A.3. Depth profile (cm) of PFCA fluxes (ng m^{-2} yr^{-1}) on the Devon Ice Cap. Values <LOD are identified in red and values <LOQ are identified in blue.

		Flux (ng m^{-2} yr^{-1})											
Depth (cm)	Year	TFA	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA
19	2015	4073	1384	26.1	<LOD	4.58	5.86	10.9	15.0	1.81	0.84	<LOD	<LOD
78	2014	14121	3224	34.7	<LOD	6.91	15.2	20.8	45.8	8.70	6.63	<LOD	<LOD
134	2013	26055	4891	88.1	<LOD	19.6	48.4	42.6	90.5	14.9	13.7	<LOD	<LOD
177	2012	33356	5438	167	33.9	38.2	86.7	54.5	118	16.7	28.6	1.19	<LOD
193	2011	10655	3195	89.7	13.7	18.8	38.7	18.6	25.6	3.19	3.60	<LOD	<LOD
235	2010	31528	10672	149	<LOD	19.6	48.0	29.4	64.6	6.50	9.43	<LOD	<LOD
280	2009	15782	7163	67.2	<LOD	10.5	28.5	28.4	43.1	7.11	8.85	<LOD	<LOD
331	2008	23604	783	121	16.7	23.6	32.6	40.9	72.1	11.3	17.0	<LOD	<LOD
363	2007	5825	36.5	28.7	<LOD	5.50	19.2	22.1	38.9	4.12	10.0	<LOD	<LOD
390	2006	14695	223	40.0	6.13	8.78	23.5	30.8	90.3	13.6	26.0	0.718	0.593
429	2005	32477	579	106	17.7	19.9	37.8	29.4	66.0	10.7	20.9	0.419	<LOD
454	2004	8472	294	59.5	9.19	9.82	20.5	23.4	45.9	7.16	7.81	<LOD	<LOD
487	2003	10733	425	38.6	8.01	7.96	19.8	15.6	29.7	4.52	7.43	<LOD	0.176
547	2002	44420	4023	171	37.0	35.4	71.0	54.5	88.9	20.8	26.1	1.68	<LOD
606	2001	9850	5846	<LOD	13.8	12.4	23.7	29.6	40.5	7.87	7.44	<LOD	<LOD
648	2000	8450	914	39.9	16.7	12.3	27.9	25.5	55.1	13.1	18.3	<LOD	<LOD
684	1999	8325	591	54.1	12.0	17.8	39.2	43.0	122	16.0	21.6	1.51	<LOD
730	1998	1953	191	19.8	<LOD	4.00	11.0	22.7	52.7	7.65	12.1	<LOD	<LOD
776	1997	3745	46.7	12.1	3.15	7.76	16.7	32.9	54.4	7.06	13.5	<LOD	<LOD
825	1996	9399	512	42.0	15.2	24.3	58.7	80.5	141	19.8	25.7	<LOD	<LOD
857	1995	5572	425	24.7	14.2	18.3	27.0	27.8	33.7	3.62	7.86	<LOD	<LOD
902	1994	8666	460	29.7	17.1	19.2	29.6	46.7	50.9	7.83	9.55	<LOD	<LOD
964	1993	10242	809	56.4	24.1	32.2	48.8	48.1	52.3	7.53	9.10	<LOD	<LOD
1006	1992	5158	1749	32.0	16.9	21.6	28.2	25.1	28.6	3.51	1.53	<LOD	<LOD
1047	1991	2640	119	35.3	15.9	16.4	28.9	35.6	42.6	7.57	8.38	<LOD	<LOD
1088	1990	2902	119	37.4	16.4	13.6	25.0	29.2	32.8	5.73	5.16	<LOD	<LOD
1144	1989	3488	71.1	18.4	4.80	13.8	26.3	29.0	44.9	5.17	9.73	<LOD	<LOD
1187	1988	2251	58.1	15.0	19.7	19.7	39.4	47.3	59.2	8.90	9.32	<LOD	<LOD
1216	1987	1759	39.4	10.2	5.44	7.67	13.3	18.7	21.2	3.96	2.89	<LOD	<LOD
1251	1986	1566	114	13.3	9.23	13.1	24.8	24.5	25.1	7.02	1.58	<LOD	<LOD
1294	1985	2479	54.7	14.1	8.33	9.41	20.9	20.0	21.4	1.33	3.81	<LOD	<LOD
1317	1984	1660	257	17.0	2.21	8.57	14.7	14.3	14.9	2.09	2.09	<LOD	<LOD
1358	1983	2117	332	14.5	3.79	7.56	14.9	18.0	17.7	1.37	<LOD	<LOD	<LOD
1394	1982	1586	346	13.6	3.56	11.6	23.3	22.0	27.4	4.08	1.62	<LOD	<LOD
1420	1981												
1458	1980												
1473	1979	666.2	244	5.3	1.38	3.21	6.79	6.56	5.59	0.50	<LOD	<LOD	<LOD
1514	1978	3103	171	15.4	4.03	12.7	30.2	22.5	31.9	3.83	1.83	<LOD	<LOD
1542	1977	1002	224	10.1	2.65	7.22	13.3	16.3	16.9	1.93	<LOD	<LOD	<LOD

Table A.4. Depth profile (cm) of PFSA fluxes (ng m^{-2} yr^{-1}) on the Devon Ice Cap. Values <LOD are identified in red.

		Flux (ng m^{-2} yr^{-1})			
Depth (cm)	**Year**	**PFBS**	**PFHpS**	**PFOS**	**FOSA**
19	2015	0.725	<LOD	5.57	<LOD
78	2014	<LOD	1.50	15.3	<LOD
134	2013	0.861	1.80	80.3	<LOD
177	2012	<LOD	<LOD	10.1	0.297
193	2011	<LOD	<LOD	6.88	<LOD
235	2010	<LOD	<LOD	4.84	<LOD
280	2009	<LOD	<LOD	4.56	<LOD
331	2008	<LOD	<LOD	6.91	<LOD
363	2007	<LOD	<LOD	3.11	<LOD
390	2006	<LOD	<LOD	3.56	<LOD
429	2005	<LOD	<LOD	4.75	0.277
454	2004	<LOD	<LOD	3.39	<LOD
487	2003	<LOD	<LOD	2.69	0.758
547	2002	<LOD	<LOD	9.57	<LOD
606	2001	<LOD	<LOD	3.03	<LOD
648	2000	<LOD	<LOD	4.43	0.266
684	1999	<LOD	<LOD	4.74	2.91
730	1998	<LOD	<LOD	5.13	9.83
776	1997	<LOD	<LOD	3.23	7.93
825	1996	<LOD	<LOD	4.76	10.1
857	1995	<LOD	<LOD	4.42	6.16
902	1994	<LOD	<LOD	7.54	16.2
964	1993	<LOD	<LOD	6.10	8.95
1006	1992	<LOD	<LOD	5.15	4.75
1047	1991	<LOD	<LOD	5.33	7.49
1088	1990	<LOD	<LOD	2.75	5.36
1144	1989	<LOD	<LOD	6.02	9.17
1187	1988	<LOD	<LOD	3.59	6.81
1216	1987	<LOD	<LOD	3.50	3.40
1251	1986	<LOD	<LOD	3.97	5.01
1294	1985	<LOD	<LOD	3.59	5.93
1317	1984	<LOD	<LOD	6.42	1.73
1358	1983	<LOD	<LOD	4.08	0.81
1394	1982	<LOD	<LOD	4.65	3.03
1420	1981				
1458	1980				
1473	1979	<LOD	<LOD	1.26	<LOD
1514	1978	<LOD	<LOD	3.44	3.18
1542	1977	<LOD	<LOD	2.11	1.56


A
2015 collection and analysis
3-year moving average
2008 collection and analysis
PFBA Flux (ng m-2)
B
PFPeA Flux (ng m-2)
C
PFHxA Flux (ng m-2)
D
PFHpA Flux (ng m-2)
1977
1978
1979
1980
1981
1982
1983
1984
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1988
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2011
2012
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2014
2015

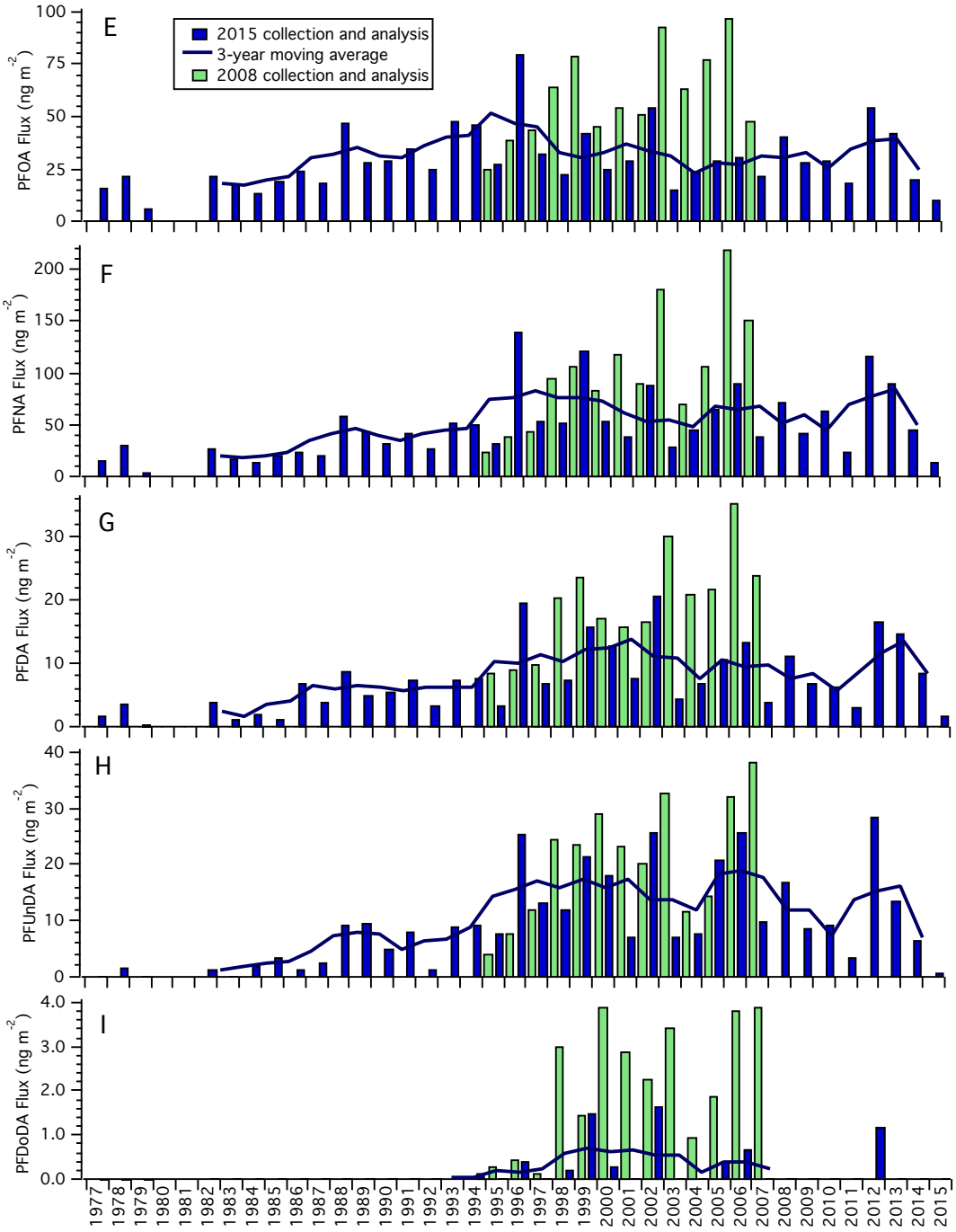

Figure A.1. Temporal flux trends for a) PFBA, b) PFPeA, c) PFHxA, d) PFHpA, e) PFOA, f) PFNA, g) PFDA, h) PFUnDA, and i) PFDoDA calculated from samples collected in 2008 (green) and 2015 (blue), along with three year moving averages for the 2015 study.

Table A.5. Reproduced EPA's 2014 Report on Percent Reductions in Emissions and Product Content of PFOA, Precursors, and Higher Homologues from U.S. Operations (cumulative percent reduction from baseline year through end of 2013).[1] Percentages in brackets refer to Canadian Percent Reductions.[2]

			% Reduction in Emissions	% Reduction in Product Content		
Company	**Reduction Year**	**Chemical Category**	**% Reductions in total quantity of chemical(s) released from baseline year**	**Fluoropolymer Dispersions**	**Other Fluoropolymers**	**Telomer based products**
Arkema	2013	PFOA, PFOA salts and Higher Homologues	91%	100%	96% (100%)	N/A
		Precursors	N/A			
Asahi	2013	PFOA, PFOA salts and Higher Homologues	100%	100% (100%)	100%	N/A (100%)
		Precursors	N/A			
Ciba/BASF	2012	PFOA	N/A			
		Higher Homologues				
		Precursors				
Clariant	2013	PFOA and PFOA salts	N/A			
		Direct Precursors				
Daikin	2013	PFOA	100%	100%	100%	100%
		Precursor and Higher Homologues	100%	N/A	N/A	100%
DuPont	2013	PFOA and PFOA salts	99.8%	99.9% (99.5%)	99.9% (99.5%)	99.9%[1] (99%)
		Higher Homologues	None Reported			
		Precursors	CBI	None Reported	None Reported	98%[1]
3M/ Dyneon	2013	PFOA, PFOA salts and Higher Homologues	100%	100%	N/A	No Telomer Production
		Precursors	No Precursor Production			
Solvay Solexis	2013	PFOA, PFOA salts and Higher Homologues	>99.999%	>99.999%	>99.999%	N/A
		Precursors	N/A			

[1]Global number – regional data are CBI (confidential business information).

Table A.6. Reproduced EPA's 2014 Report on Percent Reductions in Emissions and Product Content of PFOA, Precursors, and Higher Homologues from Non-U.S. Operations (cumulative percent reduction from baseline year through end of 2013).[1]

			% Reduction in Emissions	% Reduction in Product Content		
Company	**Reduction Year**	**Chemical Category**	**% Reductions in total quantity of chemical(s) released from baseline year**	**Fluoropolymer Dispersions**	**Other Fluoropolymers**	**Telomer based products**
Arkema	2013	PFOA, PFOA salts and Higher Homologues	CBI	N/A	CBI	N/A
		Precursors	N/A			
Asahi	2013	PFOA, PFOA salts and Higher Homologues	99.8%	100%	99.9%	Negligible as compared to precursors
		Precursors	100%	N/A	N/A	100%
Ciba/BASF	2012	PFOA	N/A			
		Higher Homologues				
		Precursors				
Clariant	2013	PFOA and PFOA salts	>80%	None Reported	None Reported	90%
		Direct Precursors	>85%	None Reported	None Reported	94%
Daikin	2013	PFOA	Not Reported			
		Precursor and Higher Homologues				
DuPont	2013	PFOA and PFOA salts	99.8%	99.9%	100%	99.9%[2]
		Higher Homologues	None Reported			
		Precursors	CBI	None Reported	None Reported	98%[2]
3M/ Dyneon	2013	PFOA, PFOA salts and Higher Homologues	100%	100%	100%	No Telomer Production
		Precursors	No Precursor Production			
Solvay Solexis	2013	PFOA, PFOA salts and Higher Homologues	N/A			
		Precursors	N/A			

[2]Global number reported.

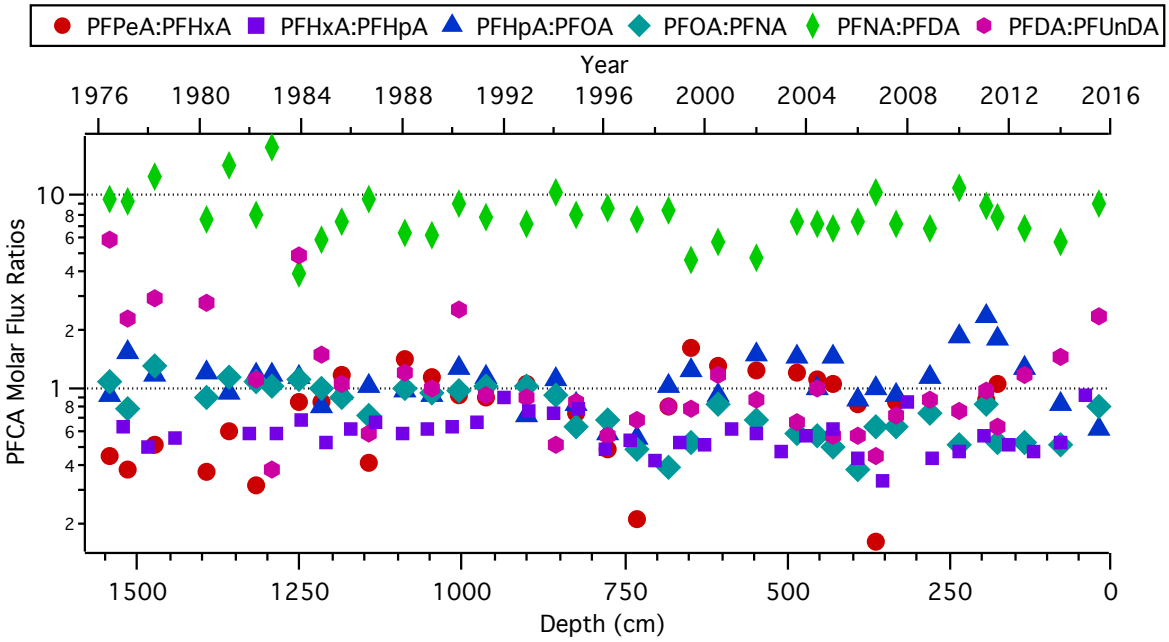

Figure A.2. Molar flux ratios for six pairs of PFCA homologues ranging from PFPeA to PFUnDA, as a function of depth and year. These pairs of PFCAs are most significant for PFHxA:PFHpA, PFHpA:PFOA, PFOA:PFNA, and PFDA:PFUnDA. These pairs of homologues have a correlation close to one suggesting that they are likely coming from similar precursor sources.

Table A.7. Depth profile (cm) of anion concentrations (µg L^{-1}) on the Devon Ice Cap. Values <LOD are identified in red and years without values were not measured due to lack of sample available.

		Concentration (µg L^{-1})									
Depth	**Year**	**Fluoride**	**Chloride**	**Nitrite**	**Nitrate**	**Sulfate**	**Phosphate**	**Acetate**	**Propionate**	**Formate**	**Butyrate**
19	2015										
78	2014	0.322	57.2	1.20	867	182	8.75	29.8	<4.06	30.4	<1.48
134	2013	0.467	51.0	1.30	616	181	9.56	<27.2	<4.06	3.68	2.69
177	2012	0.243	31.9	0.800	249	97.0	7.27	<27.2	<4.06	3.32	2.23
193	2011										
235	2010	0.341	50.2	1.40	717	229	12.0	58.8	4.65	40.9	1.90
280	2009	0.327	37.4	1.10	333	139	9.90	<27.2	<4.06	5.97	2.10
331	2008										
363	2007	0.285	21.7	0.700	156	47.9	7.88	<27.2	<4.06	2.70	<1.48
390	2006										
429	2005										
454	2004										
487	2003	0.122	26.3	0.800	288	74.4	8.75	101	4.92	50.2	3.67
547	2002	0.308	39.4	0.800	504	114	6.53	165	4.86	59.9	5.04
606	2001	0.271	39.6	0.500	414	78.8	6.53	57.0	<4.06	11.3	3.60
648	2000	0.154	29.2	0.600	320	95.5	<2.86	179	<4.06	3.07	3.67
684	1999	0.103	51.2	0.900	597	153	<2.86	418	<4.06	29.7	<1.48
730	1998	<0.079	60.3	0.600	522	96.0	8.55	<27.2	<4.06	3.15	1.57
776	1997	0.112	28.4	0.400	224	63.3	7.74	68.0	<4.06	13.4	<1.48
825	1996	0.201	36.2	0.400	336	107	6.40	70.8	<4.06	20.7	2.23
857	1995	0.210	42.8	0.800	399	117	7.20	<27.2	<4.06	2.87	4.19
902	1994	0.210	30.7	0.700	413	131	8.28	<27.2	<4.06	3.07	2.75
964	1993	0.229	42.5	0.400	530	233	9.42	89.6	4.13	37.7	5.04
1006	1992	0.243	32.7	0.700	483	218	7.67	63.2	<4.06	66.5	3.41
1047	1991	0.187	34.7	2.60	335	124	5.52	43.1	<4.06	7.33	3.21
1088	1990	0.248	36.9	0.600	171	330	7.74	<27.2	<4.06	4.07	2.55
1144	1989	0.131	32.9	0.700	381	146	6.53	76.3	<4.06	3.57	3.01
1187	1988	0.182	55.8	0.400	308	163	<2.86	<27.2	<4.06	3.26	2.29
1216	1987	0.136	25.1	0.500	408	159	6.33	149	<4.06	6.39	2.29
1251	1986	0.154	50.2	0.400	380	147	7.00	66.2	<4.06	3.43	3.21
1294	1985	0.164	17.4	0.400	165	106	8.68	<27.2	<4.06	3.12	4.45
1317	1984	<0.079	61.3	0.400	420	192	9.09	51.2	<4.06	8.87	4.52
1358	1983	0.103	41.6	0.400	277	169	9.29	46.0	<4.06	10.7	3.01
1394	1982	0.187	35.3	0.400	269	176	8.75	<27.2	<4.06	3.88	2.75
1420	1981										
1458	1980										
1473	1979										
1514	1978	0.107	42.7	0.300	410	198	7.81	<27.2	<4.06	4.94	2.88
1542	1977	<0.079	42.0	0.400	220	172	8.89	67.1	<4.06	16.2	2.23

Table A.8. Depth profile (cm) of cation concentrations (µg L^{-1}) on the Devon Ice Cap. Values <LOD are identified in red and years without values were not measured due to lack of sample available.

		Concentration (µg L^{-1})							
Depth	**Year**	**Sodium**	**Potassium**	**Calcium**	**Magnesium**	**Manganese**	**Aluminum**	**Iron**	**Silicon**
19	2015								
78	2014	65.6	35.9	702	25.3	0.984	<2.00	78.3	31.9
134	2013	60.6	22.6	786	39.7	0.775	14.6	8.34	41.2
177	2012	49.2	<20.0	742	41.8	1.15	18.4	18.5	25.0
193	2011								
235	2010	55.4	36.4	772	42.8	1.19	20.1	14.3	25.9
280	2009	40.3	30.7	592	35.1	1.09	19.9	7.91	26.8
331	2008								
363	2007	27.1	25.2	380	22.7	0.578	14.0	24.1	24.9
390	2006								
429	2005								
454	2004								
487	2003	29.9	27.3	294	10.2	0.417	9.32	6.68	27.9
547	2002	41.2	38.4	344	13.7	<0.400	14.6	5.40	27.9
606	2001	40.4	33.4	283	12.5	<0.400	9.05	3.25	23.6
648	2000	32.6	22.5	291	9.78	0.934	9.54	3.04	27.0
684	1999	69.2	31.2	478	23.1	<0.400	11.2	3.31	20.0
730	1998	64.4	63.4	363	14.7	<0.400	17.4	3.60	20.6
776	1997	24.5	<20.0	229	8.98	<0.400	9.03	3.16	21.1
825	1996	33.4	<20.0	266	12.8	<0.400	8.52	2.85	14.3
857	1995	43.3	32.4	300	13.8	<0.400	4.93	2.70	15.3
902	1994	37.2	21.1	310	15.2	<0.400	17.2	3.76	31.6
964	1993	45.7	26.3	409	13.4	<0.400	12.0	6.15	19.4
1006	1992	46.8	42.5	354	14.4	2.30	11.1	3.07	17.7
1047	1991	53.3	39.3	362	14.3	<0.400	9.89	19.2	31.4
1088	1990	81.2	<20.0	199	15.8	<0.400	14.1	2.65	26.0
1144	1989	24.3	22.5	324	11.2	<0.400	13.4	13.1	27.8
1187	1988	47.2	30.2	261	15.1	<0.400	11.3	<2.00	21.7
1216	1987	26.3	20.4	330	12.7	<0.400	16.2	3.23	18.0
1251	1986	47.7	<20.0	316	10.8	<0.400	8.88	5.96	17.4
1294	1985	13.5	<20.0	207	9.21	<0.400	7.49	2.26	21.1
1317	1984	67.7	39.6	370	21.8	0.569	26.2	8.24	21.7
1358	1983	40.8	33.3	290	13.1	<0.400	11.0	4.14	23.0
1394	1982	37.1	35.7	251	16.5	0.922	13.0	2.80	35.4
1420	1981								
1458	1980								
1473	1979								
1514	1978	51.1	23.9	326	13.8	<0.400	7.38	4.45	22.9
1542	1977	39.6	<20.0	228	13.6	<0.400	14.7	21.7	29.4

Table A.9. Coefficients of determination (R^2) and statistical significance (p) of PFAA homologues, cations and metals (n=25). Weak correlations (R^2 = 0.3 – 0.5) are shown in green and moderate correlations (R^2 = 0.5 – 0.7) in blue. Statistically significant p-values (p<0.0001) in bold.

	Sodium	Potassium	Calcium	Magnesium	Manganese	Aluminum	Iron	Silicon
	R^2= 0.055	R^2= 0.045	**R^2= 0.508**	**R^2= 0.497**	R^2= 0.091	R^2= 0.179	R^2= 0.040	R^2= 0.138
TFA	p= 0.2126	p= 0.2607	**p<0.0001**	**p<0.0001**	p= 0.1060	p= 0.0198	p= 0.2885	p= 0.0436
	R^2= 0.020	R^2= 0.029	R^2= 0.410	**R^2= 0.515**	R^2= 0.191	R^2= 0.085	R^2= 0.037	R^2= 0.034
PFPrA	p= 0.4585	p= 0.3657	p= 0.0001	**p<0.0001**	p= 0.0158	p= 0.1176	p= 0.3064	p= 0.3316
	R^2= 0.079	R^2= 0.024	**R^2= 0.481**	**R^2= 0.531**	R^2= 0.109	R^2= 0.243	R^2= 0.018	R^2= 0.079
PFBA	p= 0.1335	p= 0.4155	**p<0.0001**	**p<0.0001**	p= 0.0749	p= 0.0056	p= 0.4740	p= 0.1328
	R^2= 0.132	R^2= 0.053	R^2= 0.045	R^2= 0.019	R^2= 0.005	R^2= 0.133	R^2= 0.022	R^2= 0.064
PFPeA	p= 0.0485	p= 0.2228	p= 0.2595	p= 0.4639	p= 0.6973	p= 0.0477	p= 0.4295	p= 0.1763
	R^2= 0.218	R^2= 0.061	R^2= 0.372	R^2= 0.297	R^2= 0.069	R^2= 0.276	R^2= 0.003	R^2= 0.133
PFHxA	p= 0.0093	p= 0.1872	p= 0.0003	p= 0.0018	p= 0.1598	p= 0.0028	p= 0.7582	p= 0.0477
	R^2= 0.161	R^2= 0.015	**R^2= 0.465**	**R^2= 0.471**	R^2= 0.058	R^2= 0.251	R^2= 2.6e-04	R^2= 0.125
PFHpA	p= 0.0282	p= 0.5194	**p<0.0001**	**p<0.0001**	p= 0.2006	p= 0.0048	p= 0.9331	p= 0.0548
	R^2= 0.147	R^2= 0.009	R^2= 0.204	R^2= 0.180	R^2= 3.8e-04	R^2= 0.152	R^2= 0.007	R^2= 0.092
PFOA	p= 0.0367	p= 0.6272	p= 0.0123	p= 0.0196	p= 0.9183	p= 0.0330	p= 0.6504	p= 0.1041
	R^2= 0.130	R^2= 0.002	R^2= 0.332	R^2= 0.333	R^2= 0.006	R^2= 0.073	R^2= 9.0e-04	R^2= 0.040
PFNA	p= 0.0508	p= 0.8080	p= 0.0009	p= 0.0008	p= 0.6734	p= 0.1477	p= 0.8746	p= 0.2900
	R^2= 0.166	R^2= 0.024	R^2= 0.302	R^2= 0.241	R^2= 0.005	R^2= 0.086	R^2= 0.004	R^2= 0.112
PFDA	p= 0.0253	p= 0.4149	p= 0.0016	p= 0.0058	p= 0.7170	p= 0.1148	p= 0.7503	p= 0.0703
	R^2= 0.037	R^2= 0.003	R^2= 0.210	R^2= 0.193	R^2= 9.8e-04	R^2= 0.086	R^2= 2.2e-04	R^2= 0.034
PFUnDA	p= 0.3079	p= 0.7756	p= 0.0108	p= 0.0151	p= 0.8695	p= 0.1152	p= 0.9380	p= 0.3299
	R^2= 0.123	R^2= 0.061	R^2= 0.143	R^2= 0.128	R^2= 3.4e-04	R^2= 0.136	R^2= 6.3e-04	R^2= 0.041
PFDoDA	p= 0.0570	p= 0.1874	p= 0.0396	p= 0.0526	p= 0.9233	p= 0.0448	p= 0.8950	p= 0.2846
	R^2= 0.010	R^2= 0.086	R^2= 0.064	R^2= 0.114	R^2= 0.043	R^2= 0.007	R^2= 0.010	R^2= 0.008
PFTrDA	p= 0.6057	p= 0.1159	p= 0.1786	p= 0.0675	p= 0.2713	p= 0.6708	p= 0.6073	p= 0.6295
	R^2= 0.054	R^2= 5.8e-04	R^2= 0.301	R^2= 0.259	R^2= 0.034	R^2= 0.001	R^2= 0.081	R^2= 0.167
PFBS	p= 0.2152	p= 0.8995	p= 0.0017	p= 0.0041	p= 0.3295	p= 0.8526	p= 0.1276	p= 0.0248
	R^2= 0.053	R^2= 2.0e-06	R^2= 0.300	R^2= 0.211	R^2= 0.046	R^2= 0.039	R^2= 0.329	R^2= 0.118
PFHpS	p= 0.2212	p= 0.9940	p= 0.0017	p= 0.0107	p= 0.2545	p= 0.2937	p= 0.0009	p= 0.0628
	R^2= 0.064	R^2= 1.5e-04	R^2= 0.353	R^2= 0.329	R^2= 0.038	R^2= 0.018	R^2= 0.019	R^2= 0.214
PFOS	p= 0.1758	p= 0.9495	p= 0.0005	p= 0.0009	p= 0.3010	p= 0.4797	p= 0.4676	p= 0.0100
	R^2= 8.3e-05	R^2= 5.4e-04	R^2= 0.061	R^2= 0.112	R^2= 0.098	R^2= 0.012	R^2= 0.056	R^2= 4.4e-05
FOSA	p= 0.9618	p= 0.9034	p= 0.1879	p= 0.0703	p= 0.0922	p= 0.5677	p= 0.2083	p= 0.9723

Table A.10. Coefficients of determination (R^2) and statistical significance (p) of PFAA homologues, anions and organic acids (n=27). Weak correlations (R^2 = 0.3 – 0.5) are shown in green. Statistically significant p-values (p<0.0001) in bold.

	Fluoride	Chloride	Nitrite	Nitrate	Sulfate	Phosphate	Acetate	Propionate	Formate	Butyrate
	R^2= 0.455	R^2= 0.041	R^2= 0.126	R^2= 0.204	R^2= 6.1e-06	R^2= 0.066	R^2= 0.034	R^2= 0.320	R^2= 0.246	R^2= 0.051
TFA	**p<0.0001**	p= 0.2813	p= 0.0547	p= 0.0122	p= 0.9897	p= 0.1712	p= 0.3283	p= 0.0011	p= 0.0054	p= 0.2317
	R^2= 0.311	R^2= 0.015	R^2= 0.094	R^2= 0.113	R^2= 2.7e-04	R^2= 0.067	R^2= 0.003	R^2= 0.055	R^2= 0.051	R^2= 2.2e-04
PFPrA	p= 0.0014	p= 0.5167	p= 0.0994	p= 0.0695	p= 0.9319	p= 0.1657	p= 0.7880	p= 0.2166	p= 0.2287	p= 0.9373
	R^2= 0.306	R^2= 0.026	R^2= 0.145	R^2= 0.125	R^2= 0.007	R^2= 0.043	R^2= 0.043	R^2= 0.286	R^2= 0.215	R^2= 0.033
PFBA	p= 0.0015	p= 0.3905	p= 0.0382	p= 0.0554	p= 0.6690	p= 0.2740	p= 0.2709	p= 0.0023	p= 0.0098	p= 0.3386
	R^2= 0.162	R^2= 0.076	R^2= 0.040	R^2= 0.059	R^2= 0.051	R^2= 4.6e-04	R^2= 0.095	R^2= 0.324	R^2= 0.226	R^2= 0.350
PFPeA	p= 0.0273	p= 0.1410	p= 0.2891	p= 0.1972	p= 0.2292	p= 0.9108	p= 0.0977	p= 0.0010	p= 0.0079	p= 0.0006
	R^2= 0.383	R^2= 0.194	R^2= 0.095	R^2= 0.244	R^2= 0.141	R^2= 0.081	R^2= 0.071	R^2= 0.422	R^2= 0.292	R^2= 0.297
PFHxA	p= 0.0003	p= 0.0147	p= 0.0970	p= 0.0056	p= 0.0408	p= 0.1262	p= 0.1558	p= 0.0001	p= 0.0020	p= 0.0018
	R^2= 0.376	R^2= 0.142	R^2= 0.094	R^2= 0.166	R^2= 0.047	R^2= 0.043	R^2= 0.060	R^2= 0.308	R^2= 0.169	R^2= 0.130
PFHpA	p= 0.0003	p= 0.0400	p= 0.1000	p= 0.0256	p= 0.2515	p= 0.2724	p= 0.1920	p= 0.0014	p= 0.0239	p= 0.0505
	R^2= 0.286	R^2= 0.191	R^2= 0.072	R^2= 0.159	R^2= 0.034	R^2= 0.016	R^2= 0.074	R^2= 0.189	R^2= 0.101	R^2= 0.074
PFOA	p= 0.0023	p= 0.0158	p= 0.1522	p= 0.0290	p= 0.3289	p= 0.5063	p= 0.1460	p= 0.0163	p= 0.0867	p= 0.1455
	R^2= 0.166	R^2= 0.121	R^2= 0.077	R^2= 0.160	R^2= 1.7e-04	R^2= 0.008	R^2= 0.205	R^2= 0.072	R^2= 0.069	R^2= 9.4e-04
PFNA	p= 0.0253	p= 0.0600	p= 0.1364	p= 0.0284	p= 0.9454	p= 0.6431	p= 0.0119	p= 0.1527	p= 0.1612	p= 0.8725
	R^2= 0.278	R^2= 0.164	R^2= 0.115	R^2= 0.218	R^2= 1.8e-04	R^2= 0.011	R^2= 0.238	R^2= 0.156	R^2= 0.127	R^2= 0.020
PFDA	p= 0.0028	p= 0.0264	p= 0.0674	p= 0.0092	p= 0.9441	p= 0.5795	p= 0.0062	p= 0.0306	p= 0.0532	p= 0.4534
	R^2= 0.133	R^2= 0.030	R^2= 0.068	R^2= 0.073	R^2= 0.037	R^2= 0.027	R^2= 0.201	R^2= 0.111	R^2= 0.074	R^2= 0.003
PFUnDA	p= 0.0479	p= 0.3591	p= 0.1647	p= 0.1496	p= 0.3061	p= 0.3858	p= 0.0129	p= 0.0720	p= 0.1459	p= 0.7628
	R^2= 0.049	R^2= 0.076	R^2= 0.038	R^2= 0.114	R^2= 0.002	R^2= 0.028	**R^2= 0.492**	R^2= 0.180	R^2= 0.216	R^2= 0.026
PFDoDA	p= 0.2388	p= 0.1401	p= 0.3044	p= 0.0687	p= 0.7997	p= 0.3759	**p<0.0001**	p= 0.0194	p= 0.0096	p= 0.3903
	R^2= 0.002	R^2= 0.067	R^2= 0.001	R^2= 0.058	R^2= 0.066	R^2= 0.006	R^2= 0.012	R^2= 5.9e-04	R^2= 0.002	R^2= 0.012
PFTrDA	p= 0.8204	p= 0.1684	p= 0.8661	p= 0.1993	p= 0.1704	p= 0.6739	p= 0.5577	p= 0.8989	p= 0.7987	p= 0.5645
	R^2= 0.245	R^2= 0.048	R^2= 0.085	R^2= 0.118	R^2= 0.009	R^2= 0.031	R^2= 0.018	R^2= 0.005	R^2= 0.006	R^2= 0.008
PFBS	p= 0.0054	p= 0.2469	p= 0.1179	p= 0.0631	p= 0.6197	p= 0.3556	p= 0.4785	p= 0.6987	p= 0.6842	p= 0.6391
	R^2= 0.204	R^2= 0.048	R^2= 0.086	R^2= 0.169	R^2= 0.006	R^2= 0.022	R^2= 0.022	R^2= 0.009	R^2= 7.0e-04	R^2= 0.031
PFHpS	p= 0.0122	p= 0.2472	p= 0.1161	p= 0.0241	p= 0.6749	p= 0.4392	p= 0.4389	p= 0.6229	p= 0.8896	p= 0.3502
	R^2= 0.289	R^2= 0.057	R^2= 0.101	R^2= 0.119	R^2= 0.012	R^2= 0.045	R^2= 0.010	R^2= 1.6e-05	R^2= 0.002	R^2= 5.2e-05
PFOS	p= 0.0022	p= 0.2047	p= 0.0868	p= 0.0620	p= 0.5680	p= 0.2580	p= 0.6075	p= 0.9835	p= 0.8009	p= 0.9697
	R^2= 0.023	R^2= 0.007	R^2= 3.0e-04	R^2= 9.5e-04	R^2= 0.028	R^2= 0.013	R^2= 0.008	R^2= 3.5e-05	R^2= 0.012	R^2= 0.018
FOSA	p= 0.4283	p= 0.3286	p= 0.9276	p= 0.8713	p= 0.3760	p= 0.5445	p= 0.6362	p= 0.9754	p= 0.5658	p= 0.4771

A.1 References

1. US EPA. 2010/2015 PFOA Stewardship Program - 2014 Annual Progress Reports. (2014). at <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/20102015-pfoa-stewardship-program-2014-annual-progress>
2. ECCC. Environmental Performance Agreement. (2006). at <http://ec.gc.ca/epe-epa/default.asp?lang=En&n=AE06B51E-1>

Appendix B – Supporting Information for Chapter 4

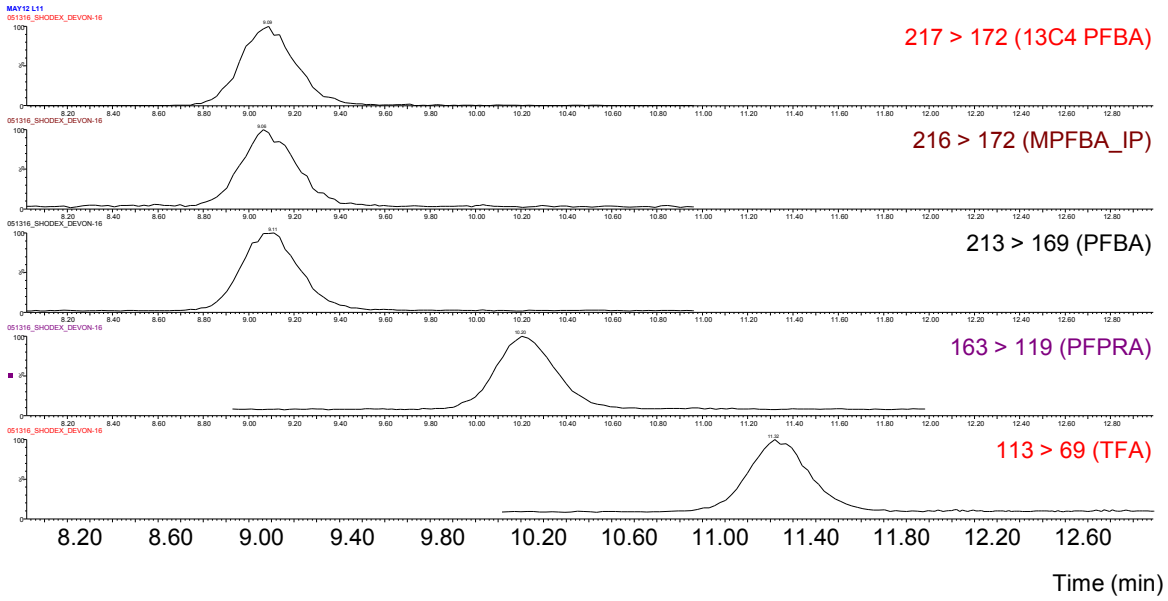

Figure B.1. LC-MS/MS Chromatogram of standard containing TFA, PFPrA, and PFBA at 4 ng/ml and isotopically labeled $^{13}C_4$-PFBA $^{13}C_3$-PFBA at 0.8 ng/ml in a 1:1 ratio of methanol-water. Precursor-product ion transitions in m/z indicated on right hand side. Note: stationary phase employed was Shodex JJ-50 RSPak, which contains quaternary ammonium groups for ion exchange hence analyte elution order.

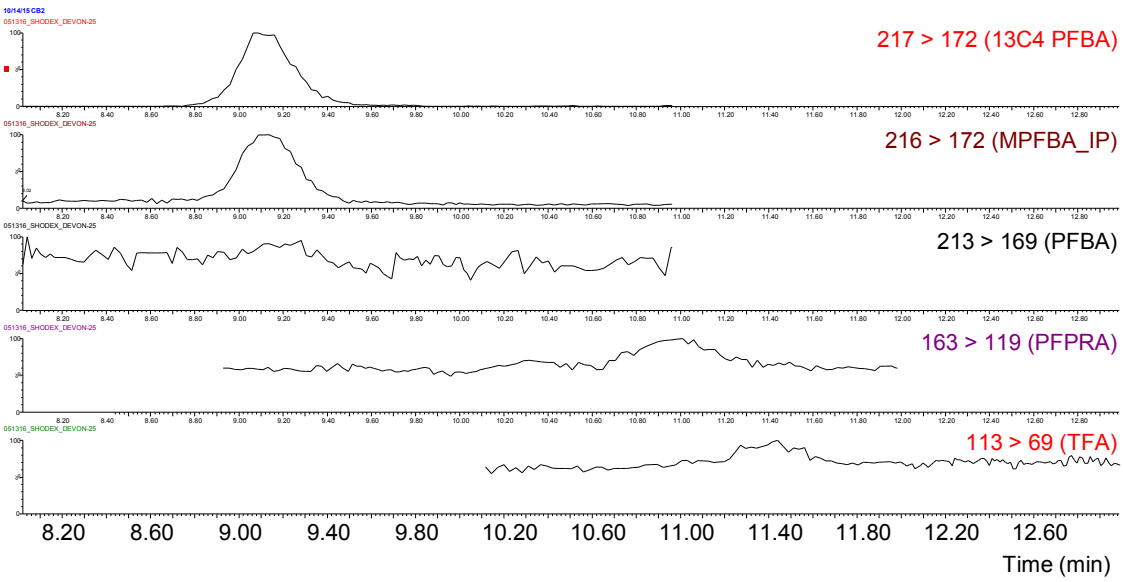

Figure B.2. LC-MS/MS chromatogram of PFBA, PFPrA, and TFA in method blank containing 0.8 ng/ml isotopically labeled $^{13}C_4$-PFBA spiked prior to extraction and 0.8 ng/ml $^{13}C_3$-PFBA spiked into the extract. Precursor-product ion transitions in m/z are indicated on the right hand side.

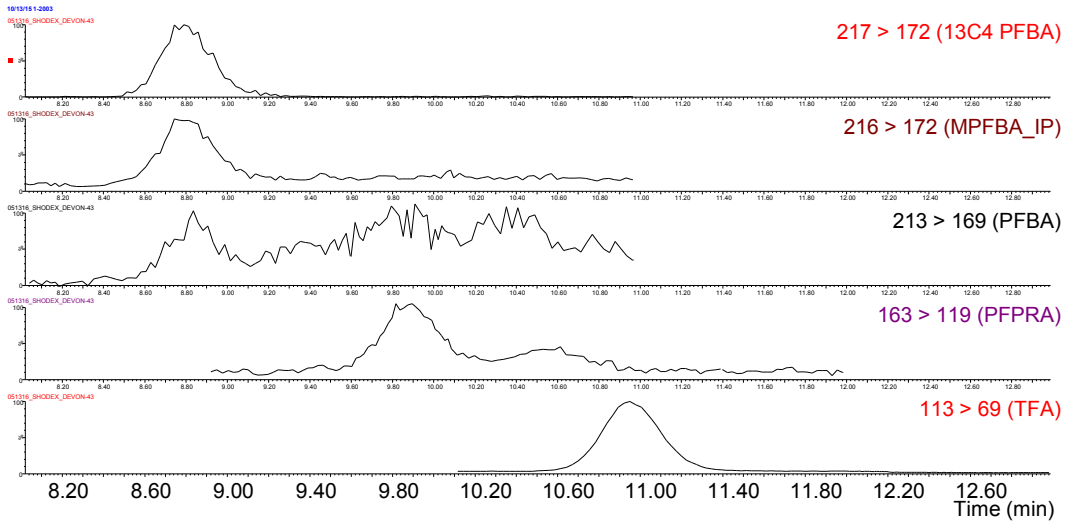

Figure B.3. LC-MS/MS chromatogram of TFA, PFPrA and PFBA in Devon Ice Cap extract corresponding to the year 2003. Isotopically labeled $^{13}C_4$-PFBA spiked into sample prior to extraction and $^{13}C_3$-PFBA spiked into extract before instrumental analysis. Precursor-product ion transitions in m/z are indicated on the right hand side. Note: Due to the higher detection limits for PFBA analysis using this column, a reverse phase C18 column was used for analysis and quantification of PFBA.

Table B.1. Depth profile (cm) of scPFCA concentrations (ng L^{-1}) and fluxes (ng m^{-2} yr^{-1}). Values <LOD are identified in red and values <LOQ are identified in blue.

		Concentration (ng L^{-1})			Flux (ng m^{-2} yr^{-1})		
Depth (cm)	**Year**	**TFA**	**PFPrA**	**PFBA**	**TFA**	**PFPrA**	**PFBA**
19	2015	38.2	13.0	0.245	4073	1384	26.1
78	2014	87.6	20.0	0.215	14121	3224	34.7
134	2013	127	23.8	0.429	26055	4891	88.1
177	2012	169	27.5	0.844	33356	5438	167
193	2011	159	47.7	1.339	10655	3195	89.7
235	2010	208	70.6	0.984	31528	10672	149
280	2009	96.0	43.6	0.409	15782	7163	67.2
331	2008	104	3.46	0.536	23604	783	121
363	2007	41.0	<0.514	0.202	5825	36.5	28.7
390	2006	123	1.86	0.335	14695	223	40.0
429	2005	198	3.53	0.646	32477	579	106
454	2004	81.9	2.84	0.575	8472	294	59.5
486.5	2003	99.1	3.92	0.356	10733	425	38.6
547	2002	151	13.7	0.581	44420	4023	171
606	2001	38.7	23.0	<0.0398	9850	5846	<LOD
648	2000	47.0	5.08	0.222	8450	914	39.9
684	1999	37.7	2.68	0.245	8325	591	54.1
730	1998	14.3	1.40	0.145	1953	191	19.8
776	1997	20.6	0.801	<0.133	3745	46.7	12.1
825	1996	38.9	2.12	0.174	9399	512	42.0
857	1995	37.3	2.84	0.165	5572	425	24.7
902	1994	41.0	2.18	0.141	8666	460	29.7
964	1993	33.9	2.68	0.187	10242	809	56.4
1005.5	1992	26.6	9.02	0.165	5158	1749	32.0
1047	1991	13.2	0.595	0.177	2640	119	35.3
1088	1990	14.4	0.591	0.186	2902	119	37.4
1144	1989	12.6	<0.514	<0.133	3488	71.1	18.4
1187	1988	9.96	<0.514	<0.133	2251	58.1	15.0
1215.5	1987	11.5	<0.514	<0.133	1759	39.4	10.2
1251	1986	7.82	0.570	<0.133	1566	114	13.3
1294	1985	11.7	<0.514	<0.133	2479	54.7	14.1
1317	1984	13.0	2.02	0.133	1660	257	17.0
1358	1983	9.69	1.52	<0.133	2117	332	14.5
1394	1982	7.72	1.68	<0.133	1586	346	13.6
1420	1981						
1458	1980						
1473	1979	8.38	3.07	<0.133	666.2	244	5.3
1514	1978	13.3	0.735	<0.133	3103	171	15.4
1542	1977	6.55	1.46	<0.133	1002	224	10.1

Table B.2. Concentration (ng L^{-1}) comparisons of TFA, PFPrA and PFBA between Devon Ice Cap and selected studies. (NM = not measured)

Site[(Reference)]	Time	Matrix	TFA	PFPrA	PFBA
Devon Ice Cap, High Arctic Canada[(This Study)]	1977-2015	Ice Core	6.55 – 208	<0.514 – 70.6	<0.040 – 1.34
Longyearbreen Glacier, Longyearbyen, Norway[1]	2006	Ice Core	NM	NM	0.080 ± 0.009
Colle Gnifetti, Swiss/Italian Alps[2]	1996-2008	Firn Core	NM	NM	0.340 – 1.83
Mt. Muztagata, Northwestern Tibetan Plateau[3]	1980-1999	Snow Core	NM	NM	<0.013
Mt. Zuoqiupu, Southeastern Tibetan Plateau[3]	1996-2007	Snow Core	NM	NM	<0.013 – 0.056
Lake Namco, Southern Tibetan Plateau[3]	2010	Surface Snow	NM	NM	0.913 – 2.57
Longyearbreen Glacier, Longyearbyen, Norway[1]	2006	Surface Snow	NM	NM	0.108 ± 0.045
Switzerland (Urban to Alpine) [4]	1996-1997	Rain & Snow	<3.00 – 1550	NM	NM
Baikal, Siberia[4]	1996	Rain & Snow	30.0 – 215	NM	NM
Kejimkujik, Nova Scotia – Remote[5]	2002	Precipitation	4.00 – 100	<0.100 – 59.0	<0.100 – 2.90
Algoma, Ontario - Remote[5]	2002	Precipitation	8.00 – 220	1.20 – 36.0	0.500 – 11.0
Switzerland (Alpine Mountain Lakes) [4]	1997	Lake Water	46.0 – 360	NM	NM
Baikal, Siberia[4]	1996	Lake Water	12.0 – 35.0	NM	NM
Canada Basin, Western Arctic[6]	1998	Ocean Water	34.0 – 181	NM	NM
Nares Strait, Eastern Arctic[6]	1998	Ocean Water	8.00 – 170	NM	NM
Arctic Ocean[7]	2010	Sea Ice Core & Snow	NM	NM	<0.130 – 1.00
Arctic Ocean[7]	2010	Marine Surface Water	NM	NM	<0.130 – 0.360
North Atlantic Ocean[8]	1995	Marine Surface Water	70.0 - 250	NM	NM

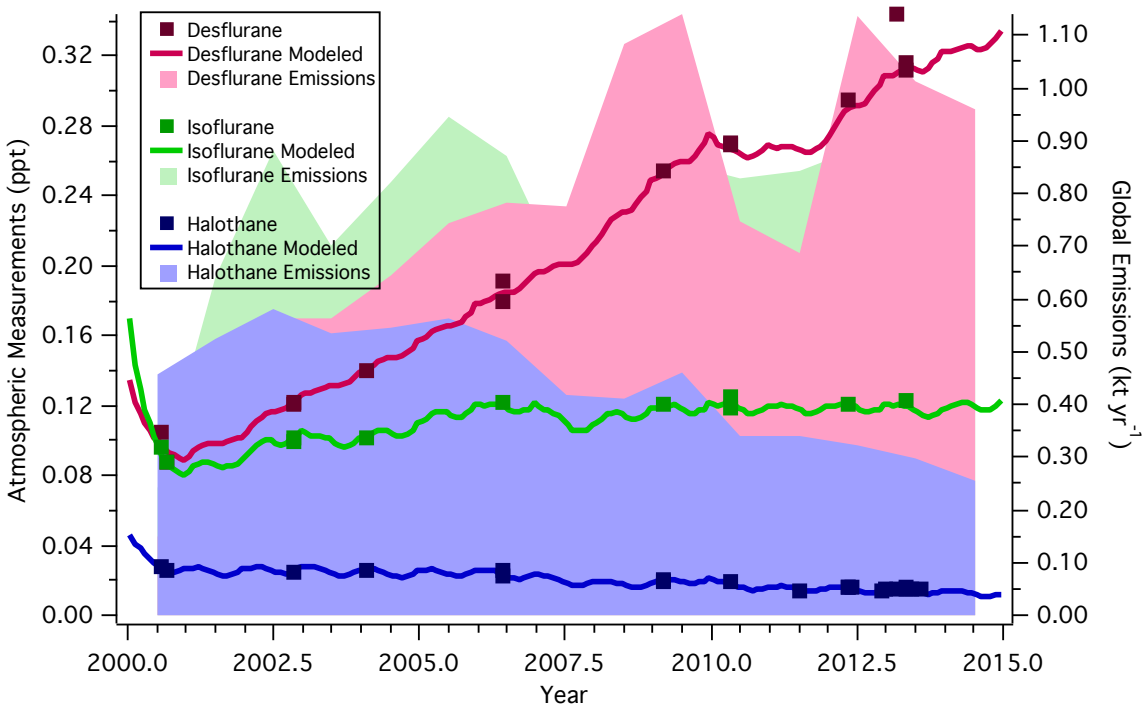

Figure B.4. Atmospheric measurements and global emissions of halogenated anaesthetics. Desflurane and isoflurane atmospheric measurements are model-derived for the Northern Polar Hemisphere (solid lines) and are measured (squares) for four northern sites (Niwot Ridge, Junfraujoch, Mace Head and La Jolla). Halothane atmospheric measurements are model-derived for the Northern Polar Hemisphere (solid line) and are measured (squares) for six northern sites (Niwot Ridge, Junfraujoch, Mace Head, La Jolla, Dubendorf and Rigi-Seebodenalp). Desflurane and halothane global emissions are model-derived.[9]

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